Supporting Information for

Enolesters as chain end-functionalizing agents for the living ring opening metathesis polymerization

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Experimental

^{1}H NMR reaction of **G1** benzylidene with *cis/trans*-**BAc** as terminating agent

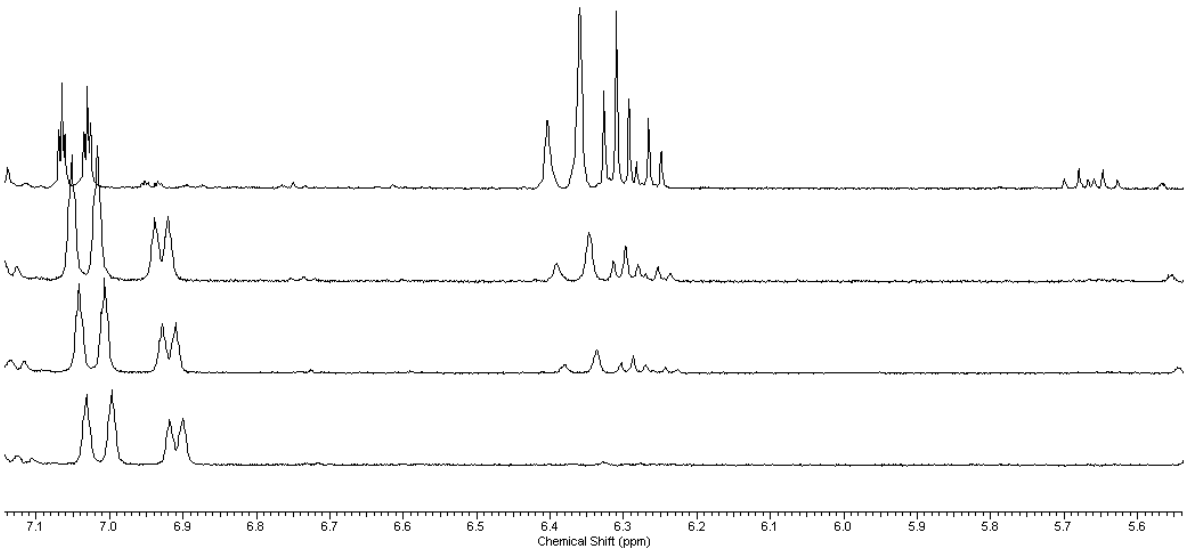

Figure S1 Reaction between **G1** and but-1-en-1-yl acetate **(BAc)**. Spectra from bottom to top: 0h, 3h, 6h and 96h. For clarity the full spectral window is not shown. Carbene signals from the residual initiator complex (20.01 ppm in ^{1}H NMR spectra in methylene chloride-d_2, 400 MHz) are present at all times. *trans*- But-1-en-1-yl acetate at 7.05 ppm (d, J = 12.7 Hz), *cis*-but-1-en-1-yl acetate at 6.94 ppm (d, J = 6.7 Hz), *(Z/E)*-but-1-en-1-ylbenzene at 6.38 ppm (d, J = 16.1 Hz, *E/Z* = 87:13).

Table S1 Ring-opening Metathesis Polymerization of Different Monomers with Different Catalysts and Terminating-Agents (TA).

Entry	Monomer	Catalyst	Terminating agent	Mon:Cat:TA	$M_{n,theo}$[kDa]	$M_{n,exp}$[kDa]	PDI
1[a]	**MNI**	**G1**	vinyl acetate	17:1:50	3000	5400	1.23
2[a]	**MNI**	**G1**	vinyl ether	17:1:50	3000	5300	1.26
3[a]	**MNI**	**G1**	**1**	17:1:50	3000	5800	1.21
4[a]	**MNI**	**G1**	**4**	10:1:5	1800	3900	1.12
5[a]	**MNI**	**G1**	**4**	20:1:5	3500	5400	1.18
6[a]	**MNI**	**G1**	**4**	30:1:5	5300	6800	1.18
7[a]	**MNI**	**G1**	**6**	20:1:5	3500	5800	1.18
8[a]	**HNI**	**G1**	**4**	20:1:5	3500	5200	1.16
9[a]	**OMNI**[c]	**G1**	**4**	20:1:5	3500	3200	1.11
10[b]	**MNI**	**G3**	**4**	10:1:5	1800	2500	1.11
11[b]	**MNI**	**G3**	**4**	20:1:5	3500	6500	1.17
12[b]	**MNI**	**G3**	**4**	30:1:5	5300	11300	1.15

[a] Mn were obtained from GPC in THF vs polystyrene standards, RI detector.

[b] Mn were obtained from GPC in Chloroform vs polystyrene standards, RI detector and the produce for synthesizing **Polymers 10-12** is the same with **Polymers 4-6**.

[c] *Exo*-*N*-methyl-7-oxanorbornene-2,3-dicarboximide

Table S2 Time-resolved termination reaction of **MNI** and **4** with **G1** in CD_2Cl_2[a] followed by ^{1}H NMR spectroscopy.

Eq.	5min	10min	20min	30min	40min	50min	60min	90min	120min
1eq	4.40	1.90	1.12	0.64	0.47	0.22	0.1	0	0
5eq	0.11	0	0	0	-	-	-	-	-
10eq	0	0	0	0	-	-	-	-	-
20eq	0	0	0	0	-	-	-	-	-

[a] **G1** (8.23 mg) was dissolved in 0.5 ml CD_2Cl_2, then **MNI** (10 mg) was added. After 1h, terminating agent **4** (dissolved in 0.1 ml of CD_2Cl_2) was added at t_0. The concentration of the propagating Ru carbene signal (^{1}H-NMR, 400 MHz) was integrated with respect to residual protonated solvent. "0" indicates that no propagating Ru carbene peak was observed and "-" means the data point was not recorded.

NMR Spectra

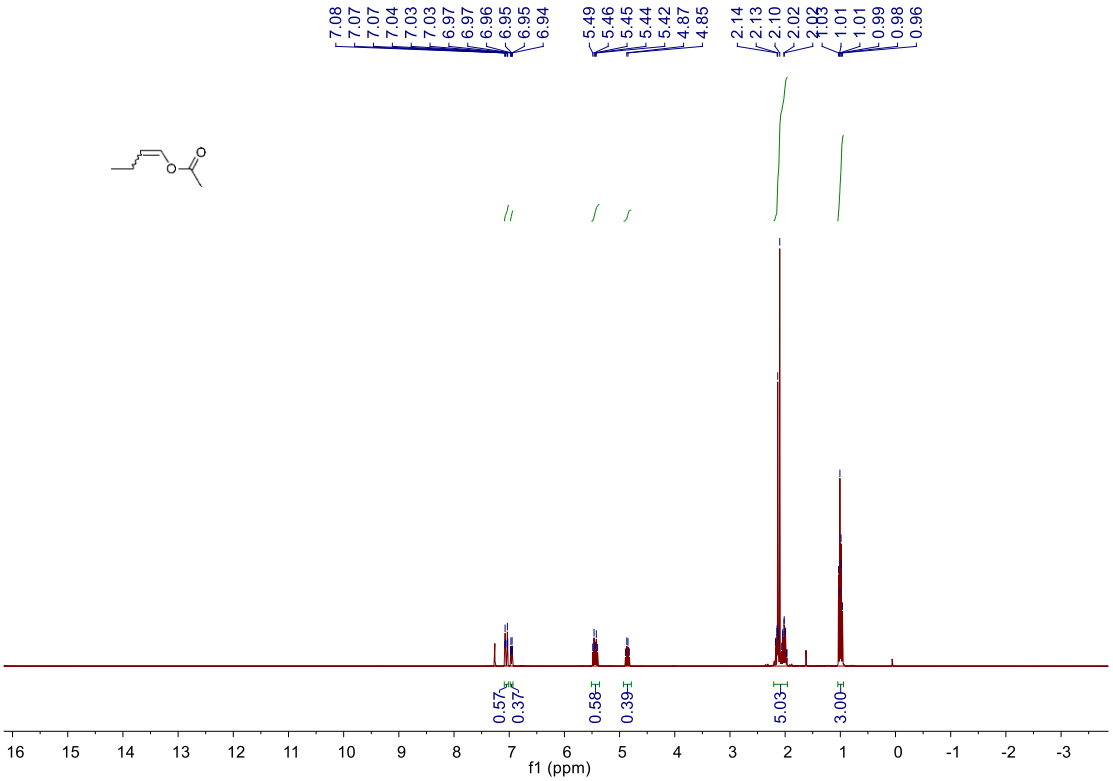

Figure S2 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of **1**

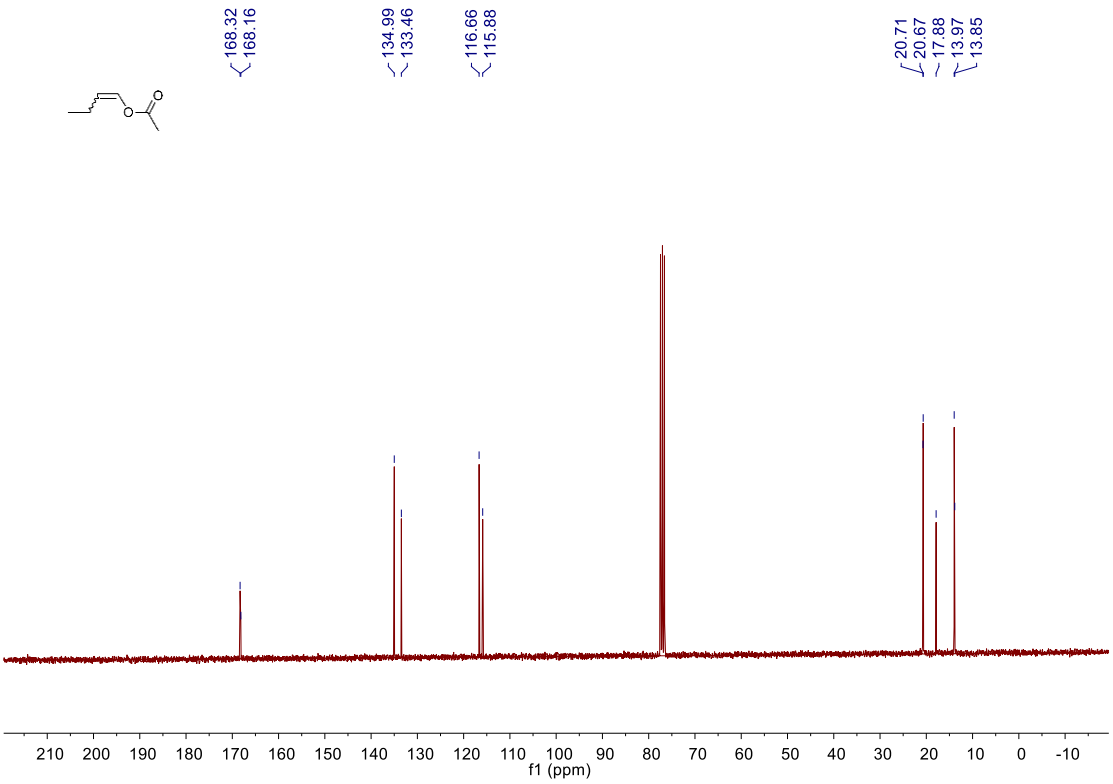

Figure S3 ^{13}C-NMR spectrum (75 MHz, $CDCl_3$) of **1**

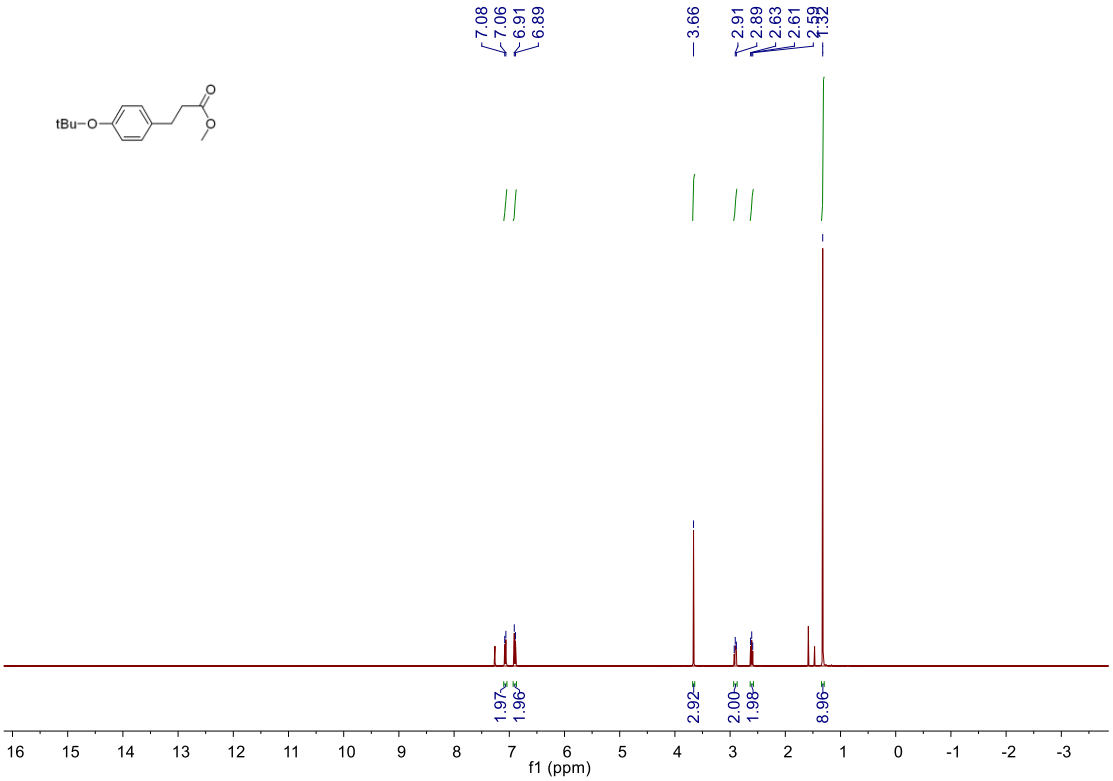

Figure S4 ^{1}H-NMR spectrum(400 MHz, $CDCl_3$) of **2**

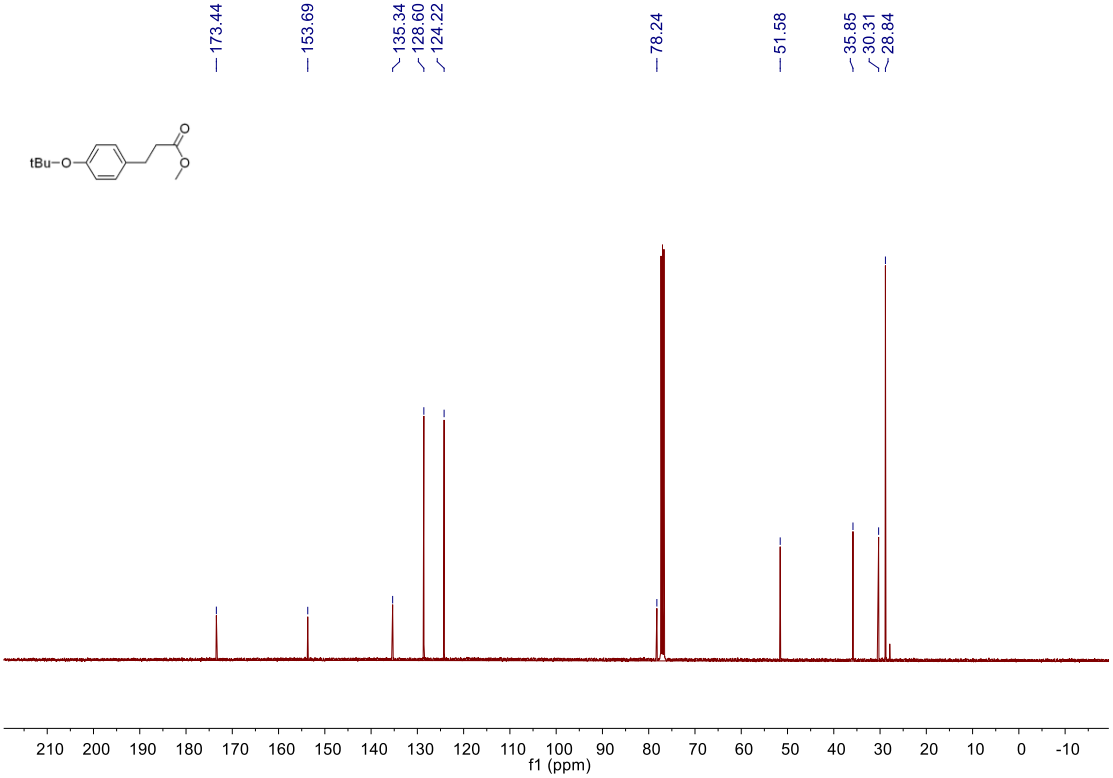

Figure S5 ^{13}C-NMR spectrum(101 MHz, $CDCl_3$) of **2**

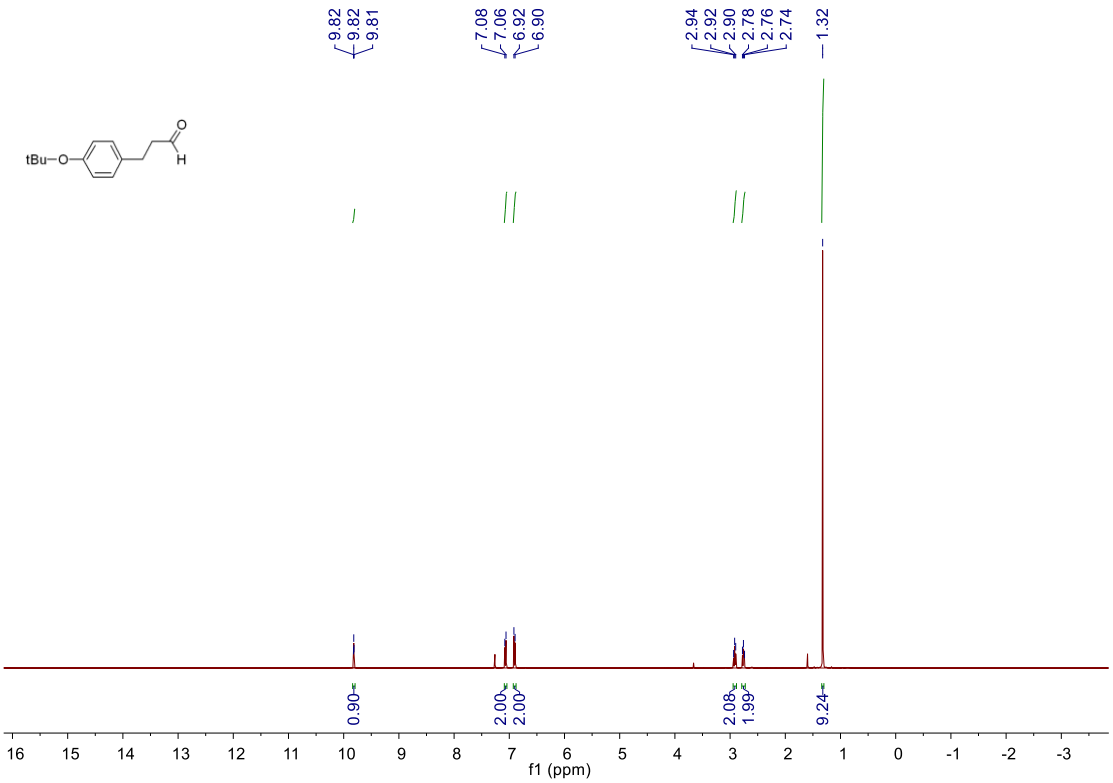

Figure S6 ^{1}H-NMR spectrum(400 MHz, $CDCl_3$) of **3**

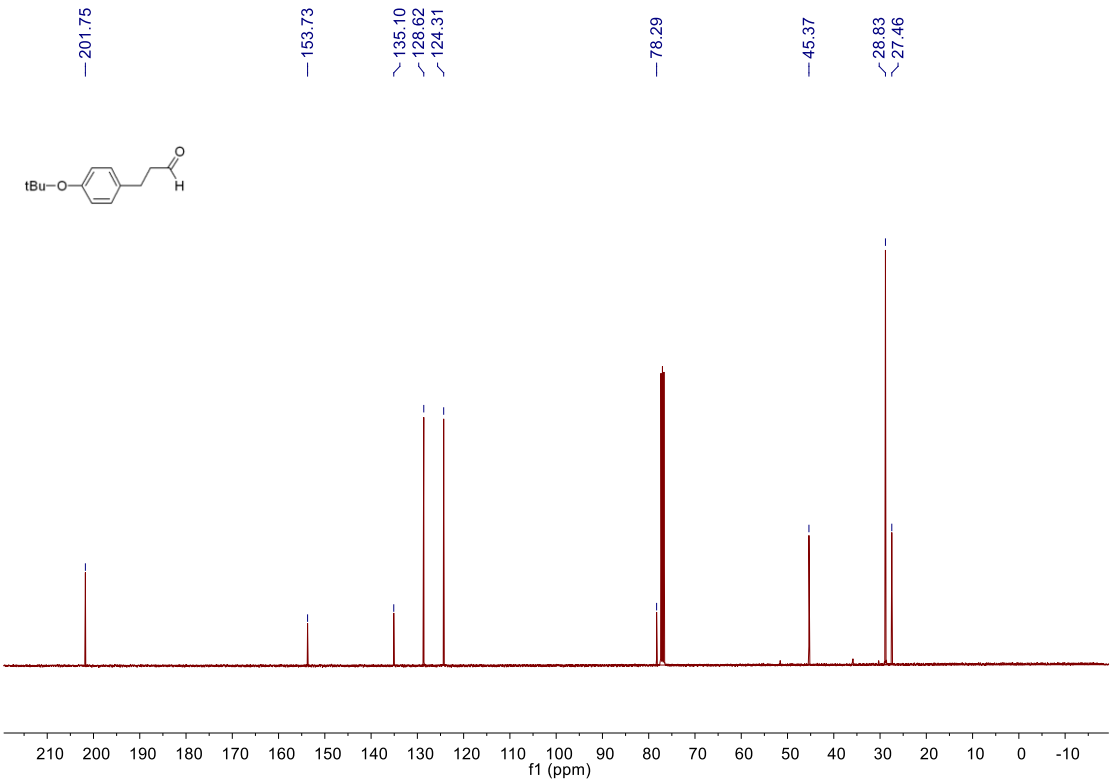

Figure S7 ^{13}C-NMR spectrum(101 MHz, $CDCl_3$) of **3**

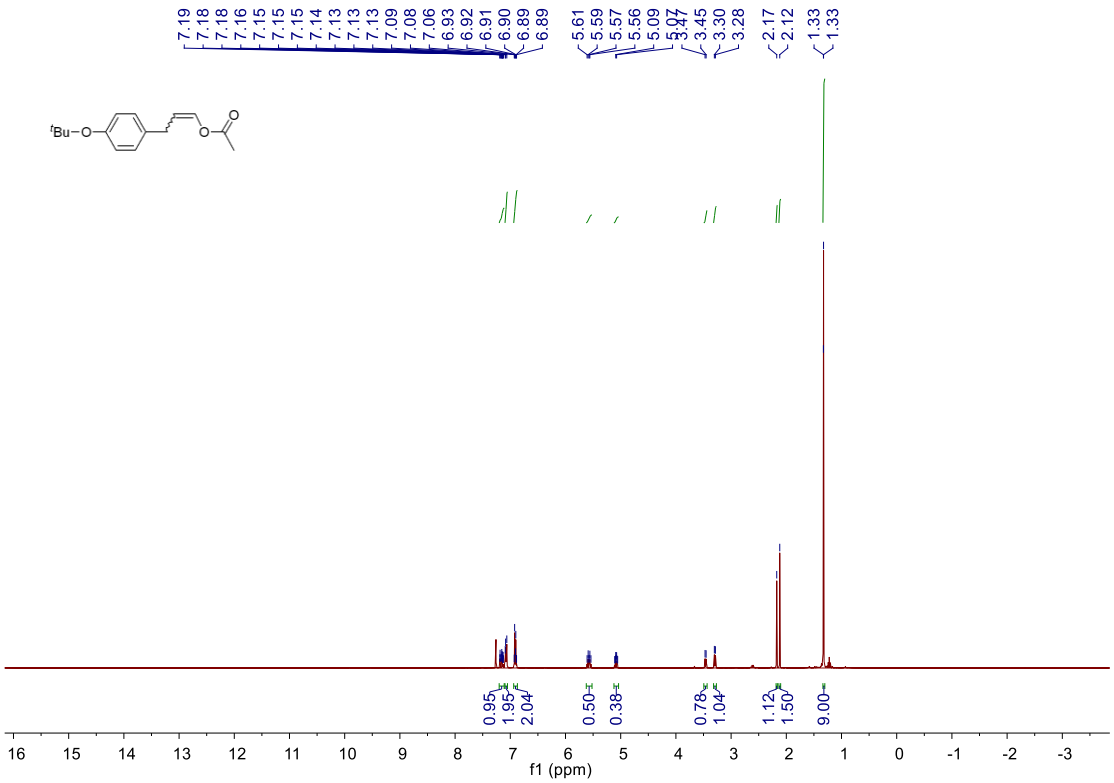

Figure S8 ^{1}H-NMR spectrum(400 MHz, $CDCl_3$) of **4**

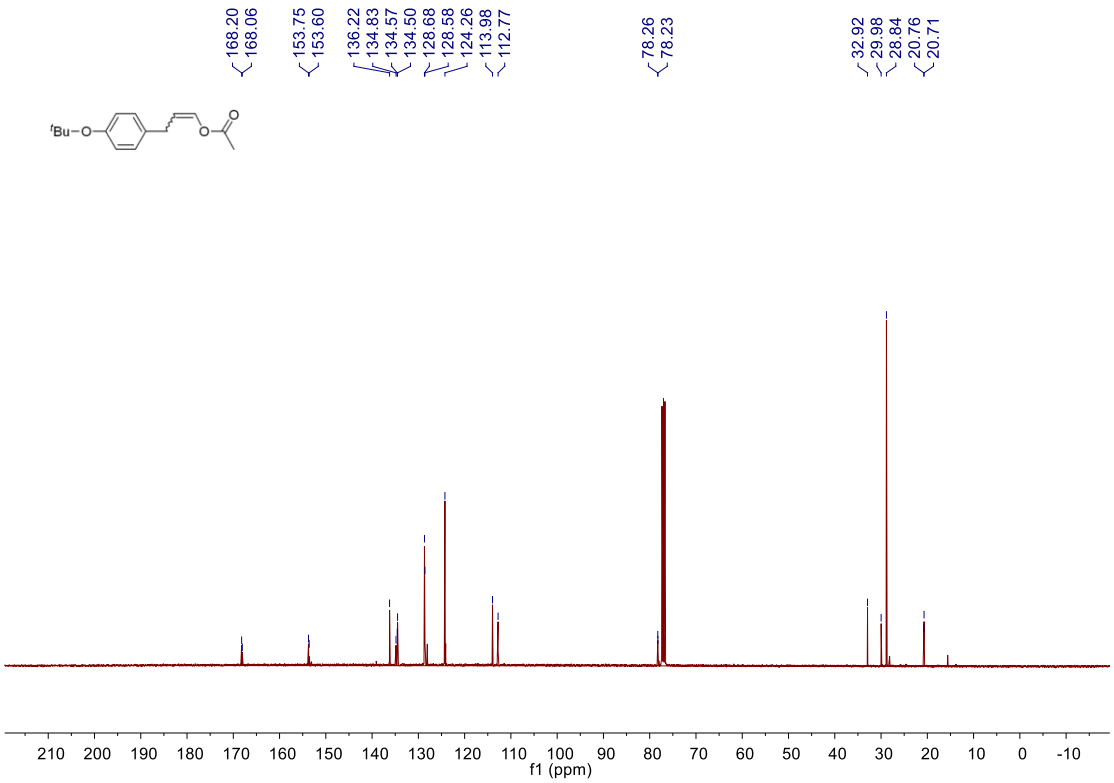

Figure S9 ^{13}C-NMR spectrum(101 MHz, $CDCl_3$) of **4**

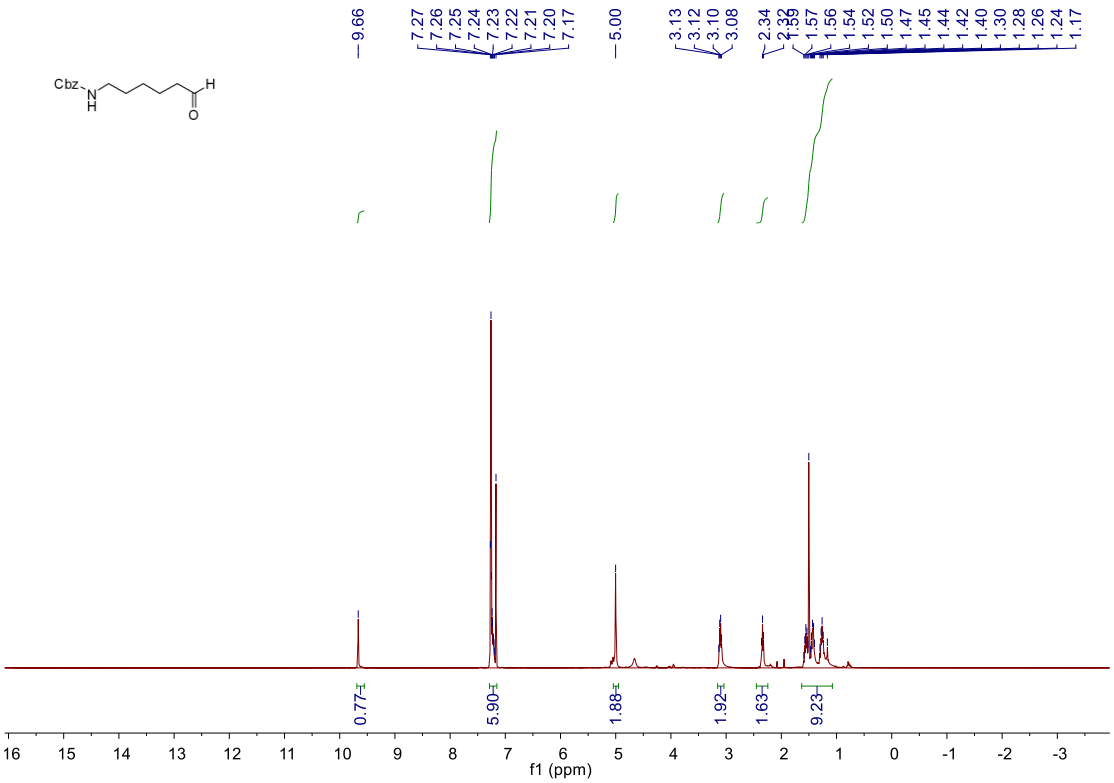

Figure S10 ^{1}H-NMR spectrum(400 MHz, $CDCl_3$) of **5**

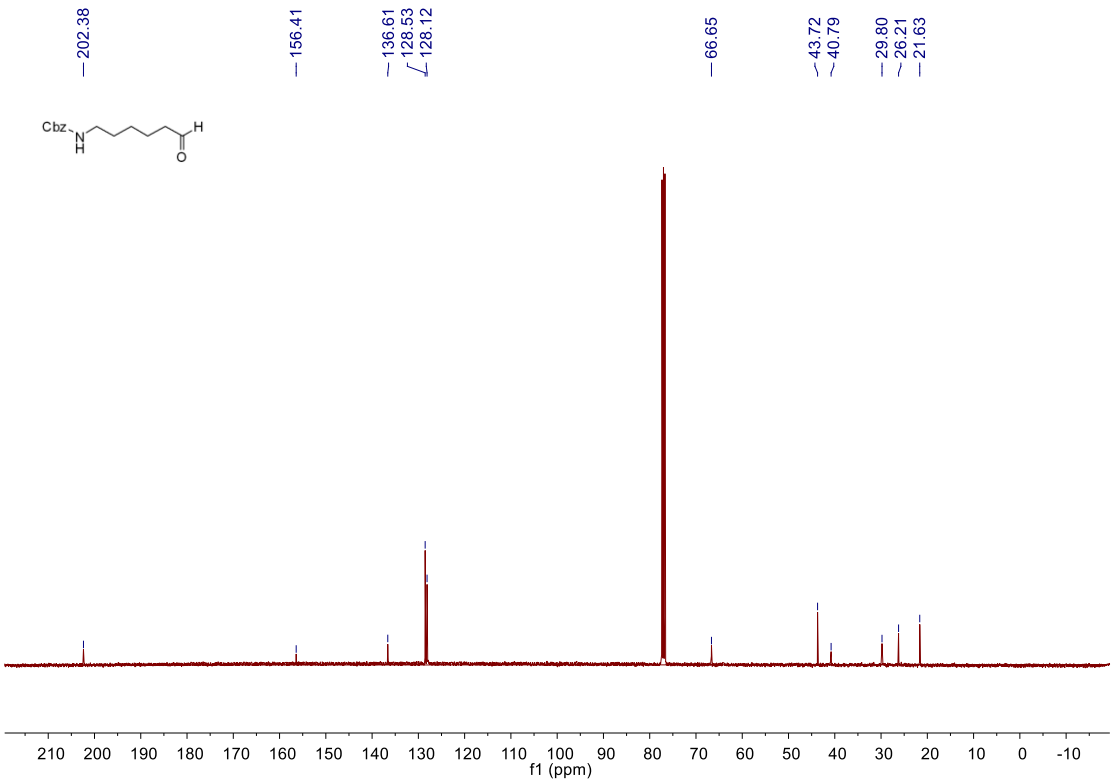

Figure S11 ^{13}C-NMR spectrum(101 MHz, $CDCl_3$) of **5**

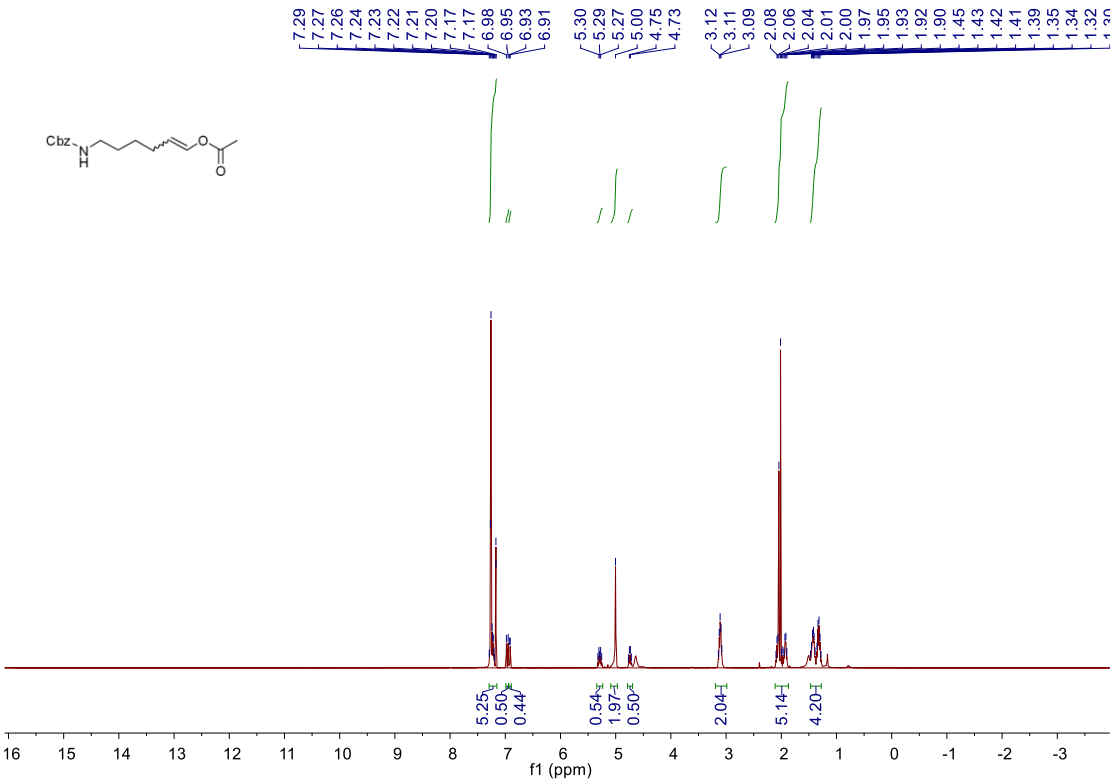

Figure S12 ^{1}H-NMR spectrum(400 MHz, $CDCl_3$) of **6**

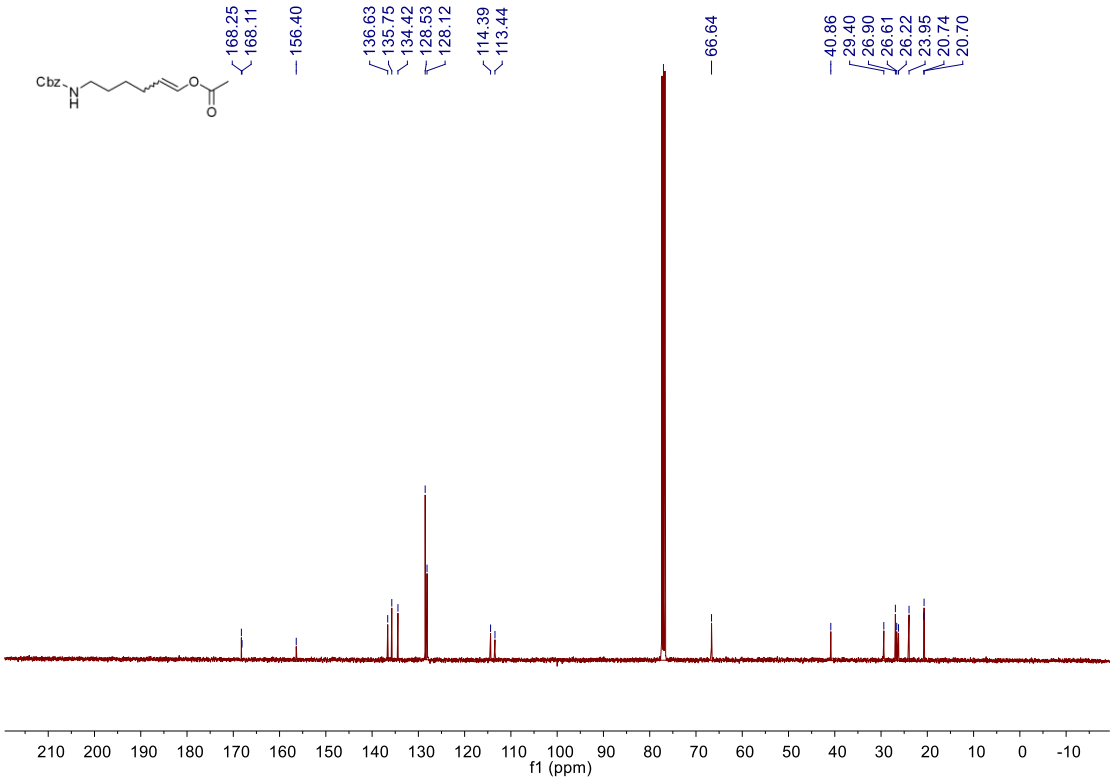

Figure S13 ^{13}C-NMR spectrum(101 MHz, $CDCl_3$) of **6**

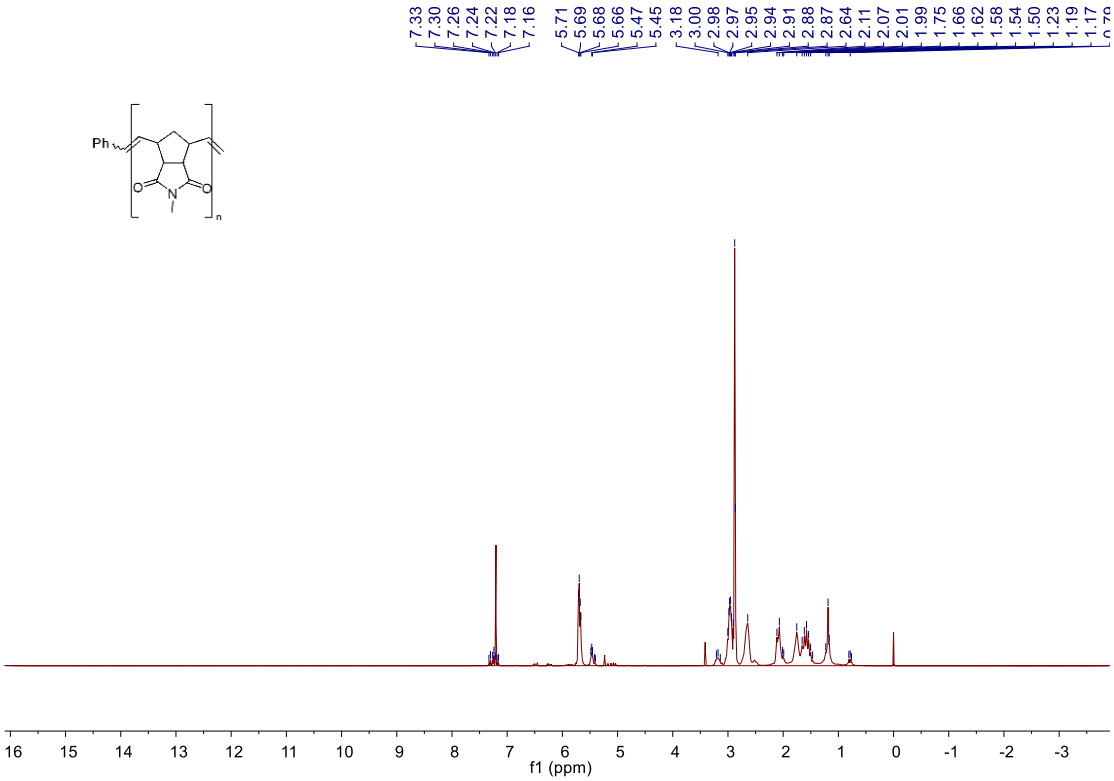

Figure S14 ^{1}H-NMR spectrum(300 MHz, $CDCl_3$) of **Polymer 1**

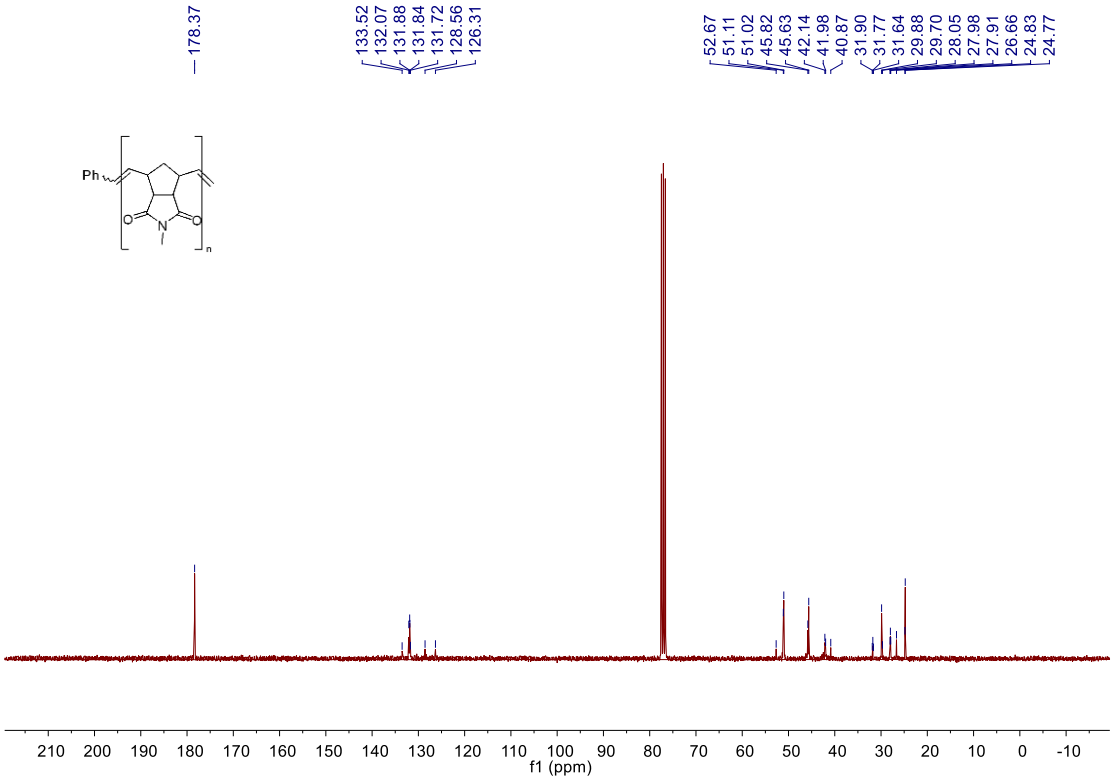

Figure S15 ^{13}C-NMR spectrum(75 MHz, $CDCl_3$) of **Polymer 1**

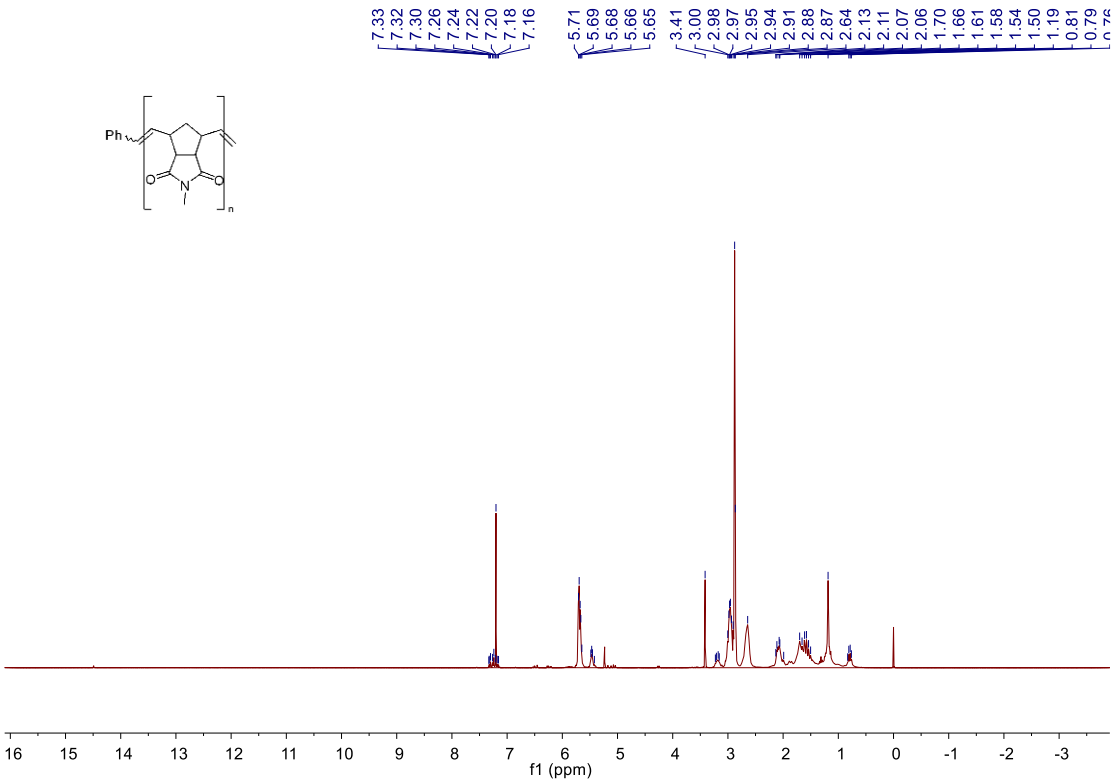

Figure S16 ^{1}H-NMR spectrum(300 MHz, $CDCl_3$) of **Polymer 2**

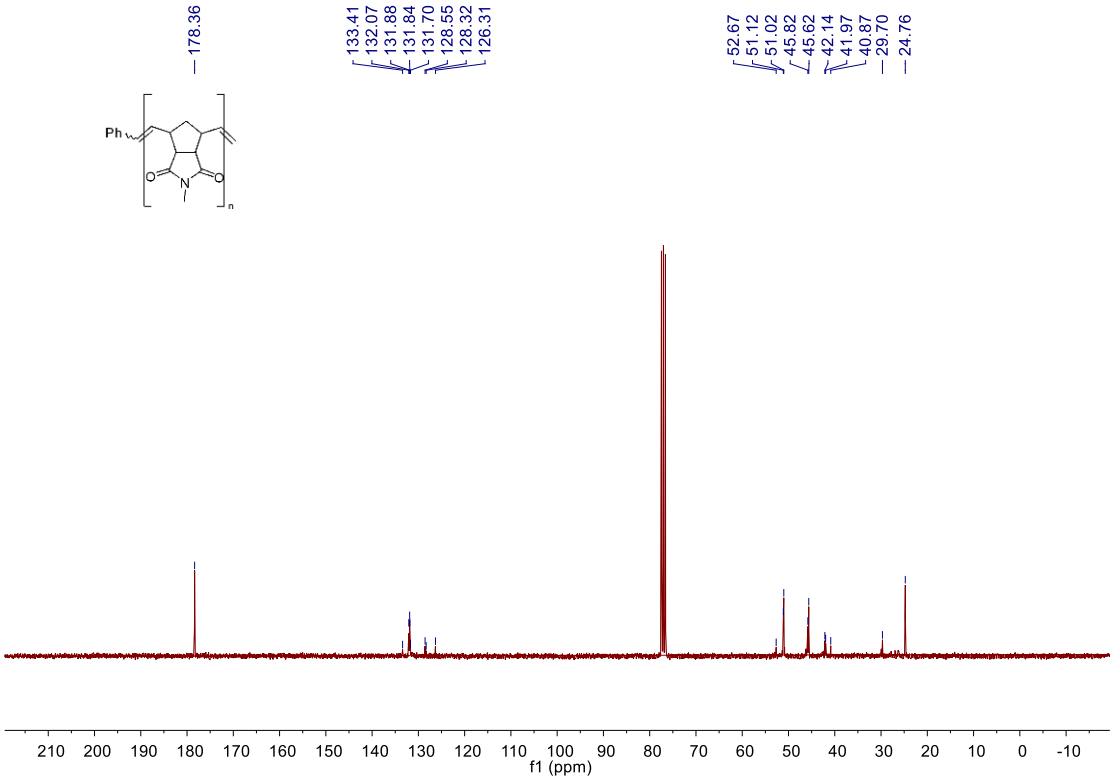

Figure S17 ^{13}C-NMR spectrum(75 MHz, $CDCl_3$) of **Polymer 2**

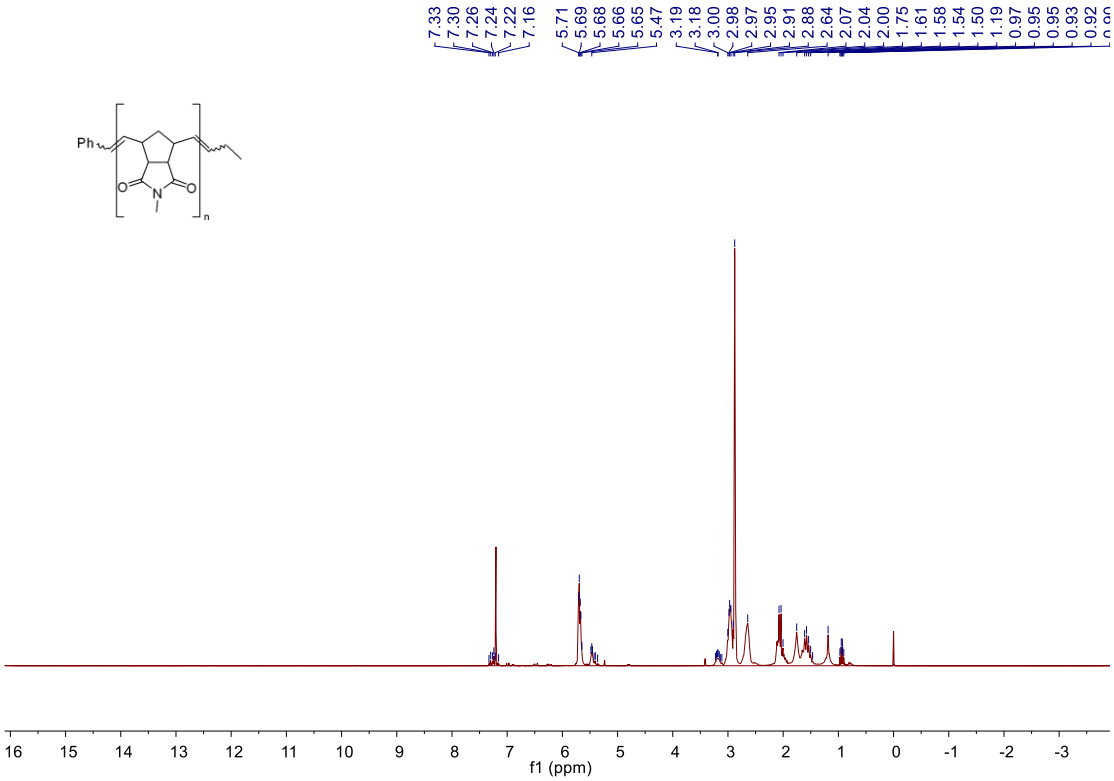

Figure S18 ^{1}H-NMR spectrum(300 MHz, $CDCl_3$) of **Polymer 3**

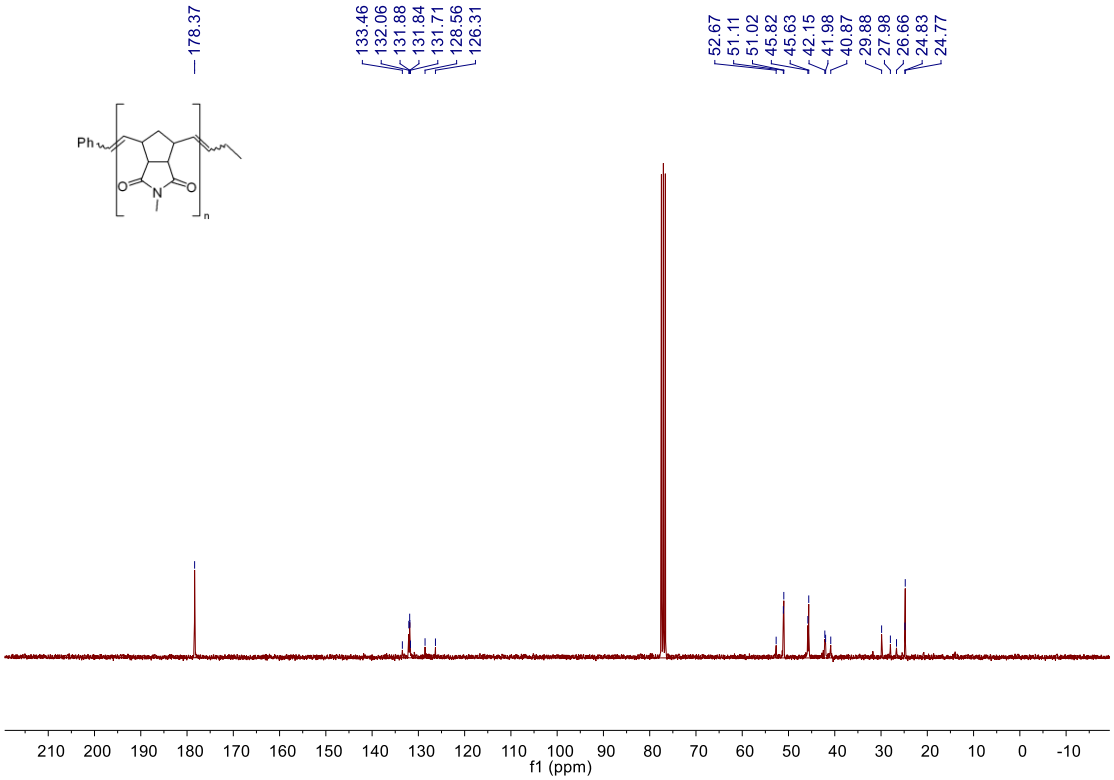

Figure S19 ^{13}C-NMR spectrum(75 MHz, $CDCl_3$) of **Polymer 3**

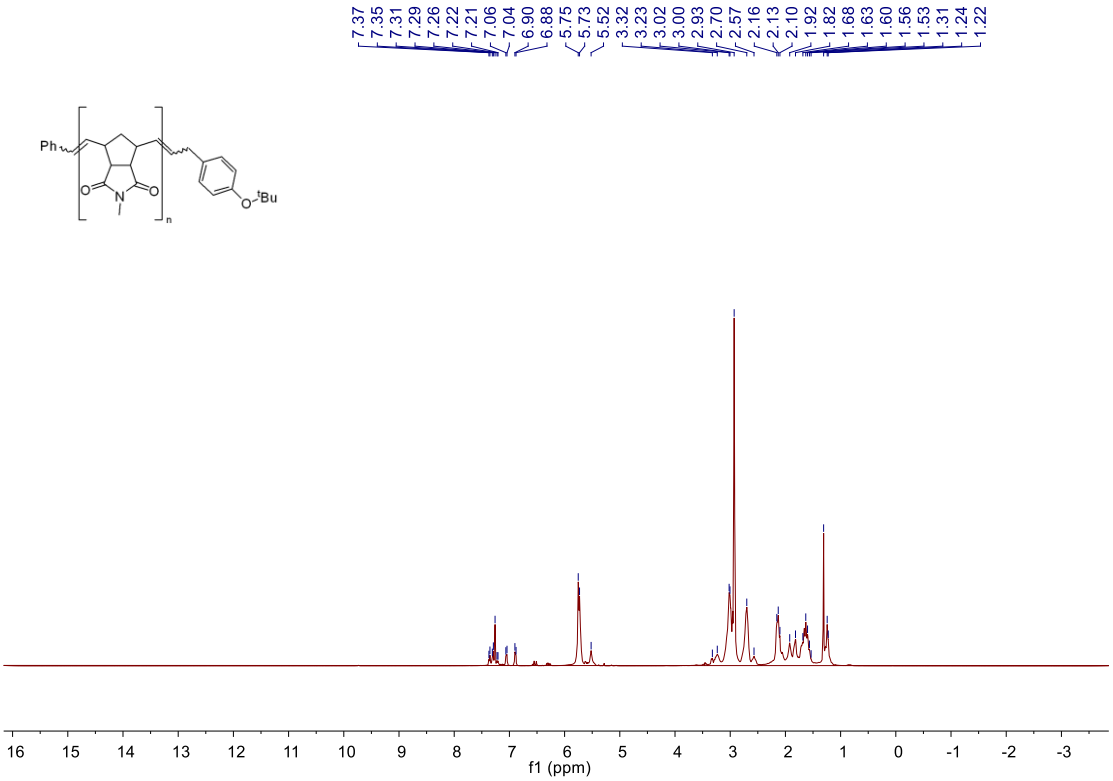

Figure S20 ^{1}H-NMR spectrum(400 MHz, $CDCl_3$) of **Polymer 4**

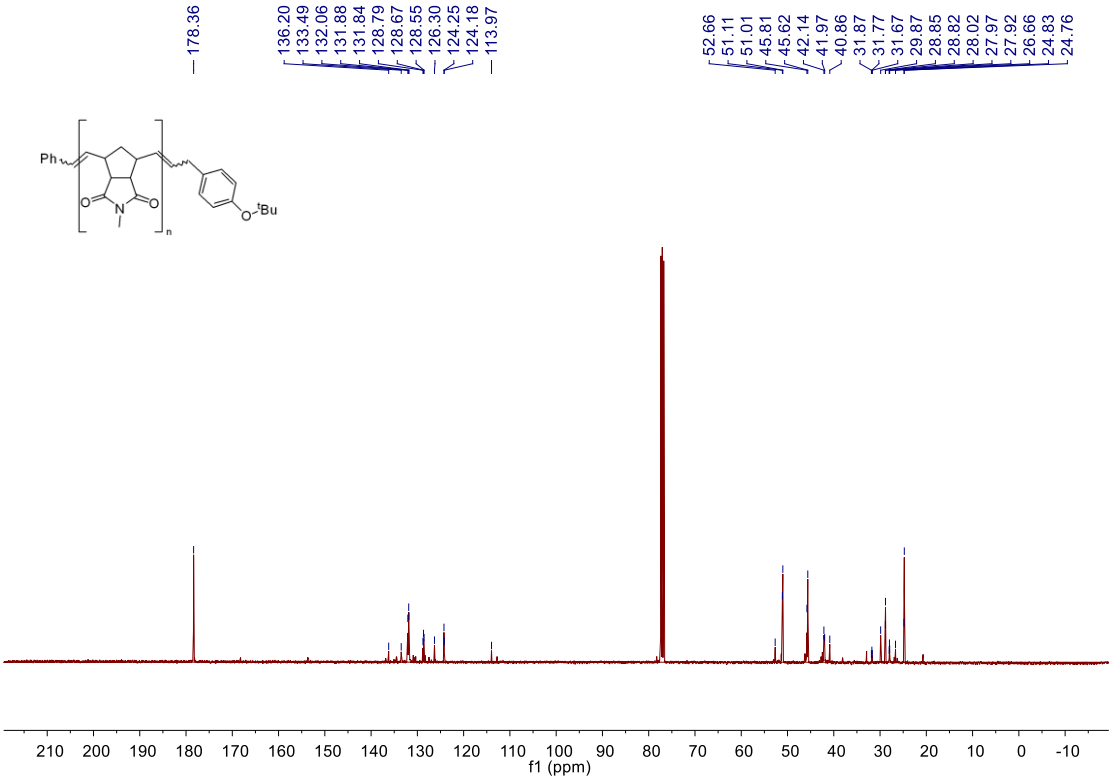

Figure S21 ^{13}C-NMR spectrum(101 MHz, $CDCl_3$) of **Polymer 4**

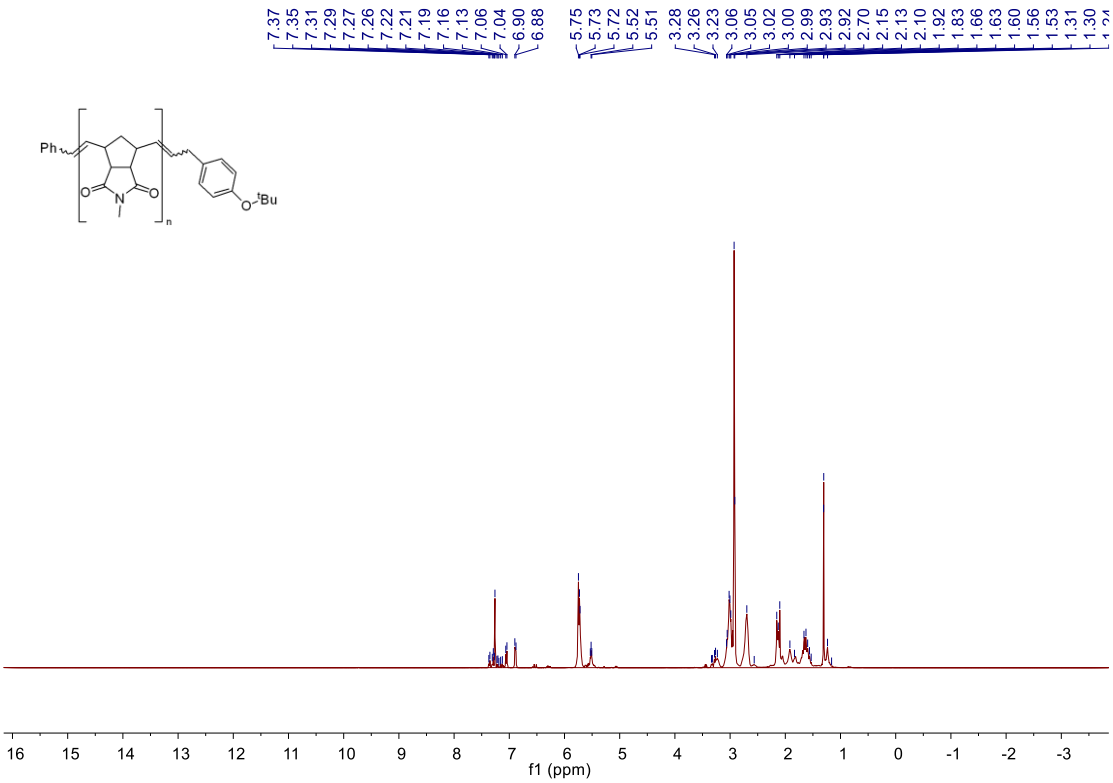

Figure S22 ^{1}H-NMR spectrum(400 MHz, $CDCl_3$) of **Polymer 5**

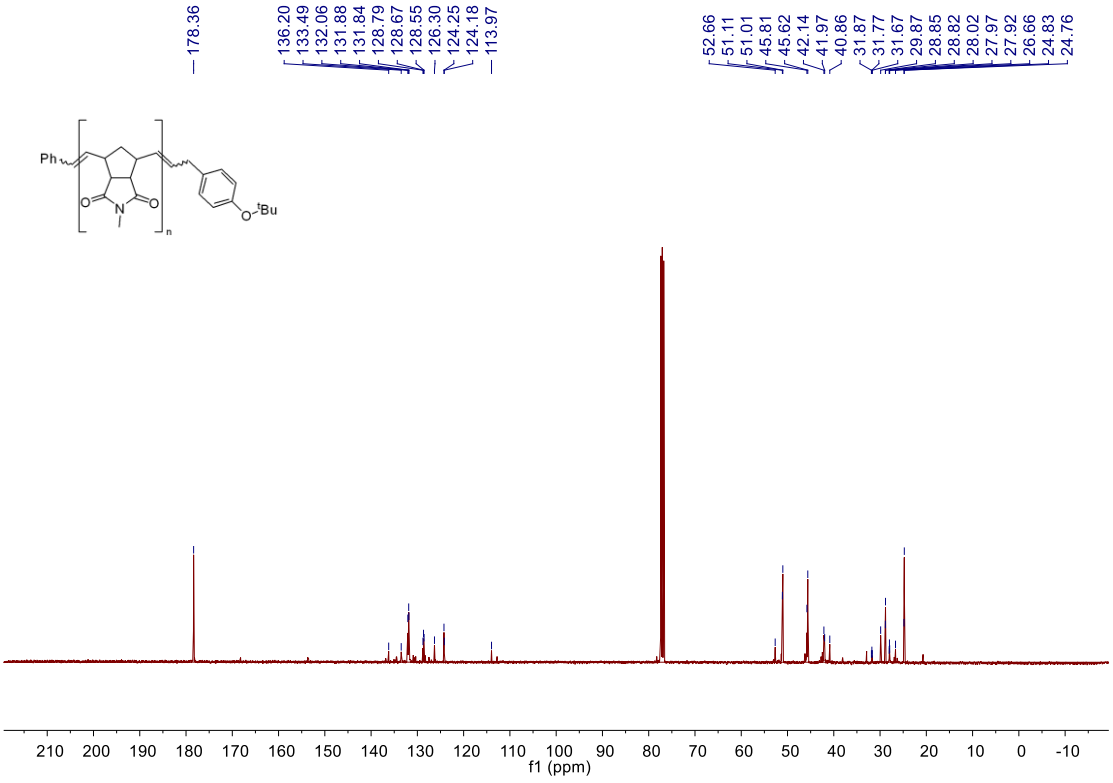

Figure S23 ^{13}C-NMR spectrum(101 MHz, $CDCl_3$) of **Polymer 5**

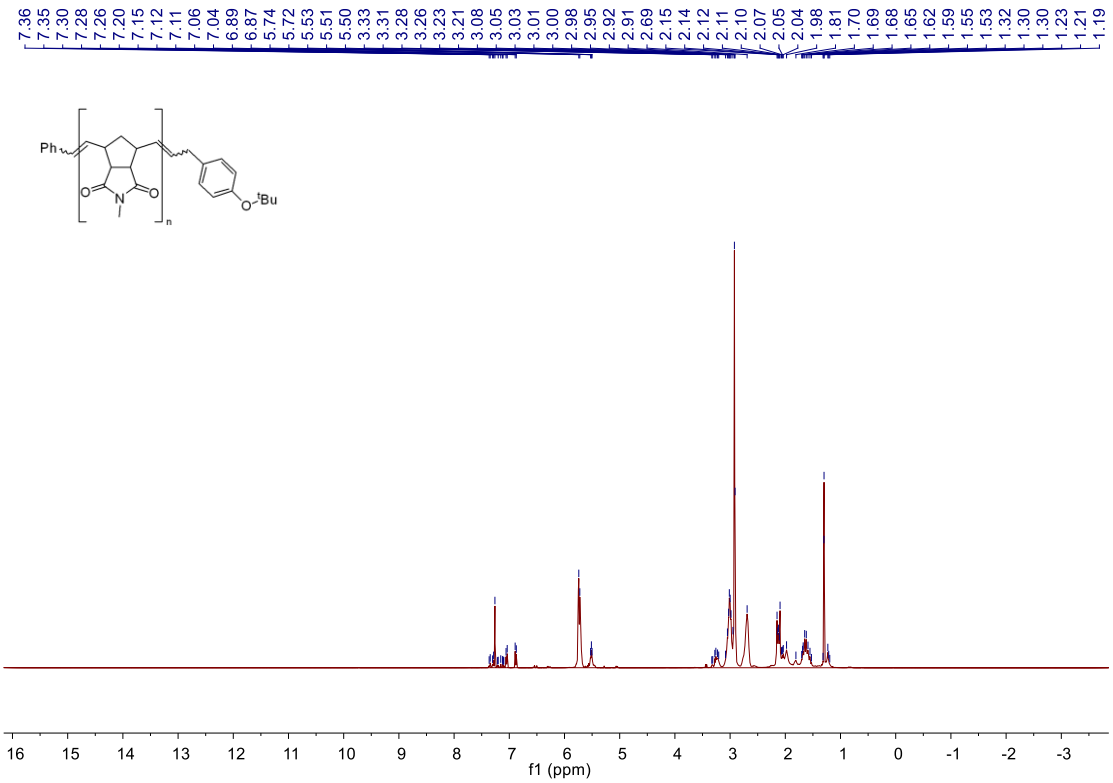

Figure S24 ^{1}H-NMR spectrum(400 MHz, $CDCl_3$) of **Polymer 6**

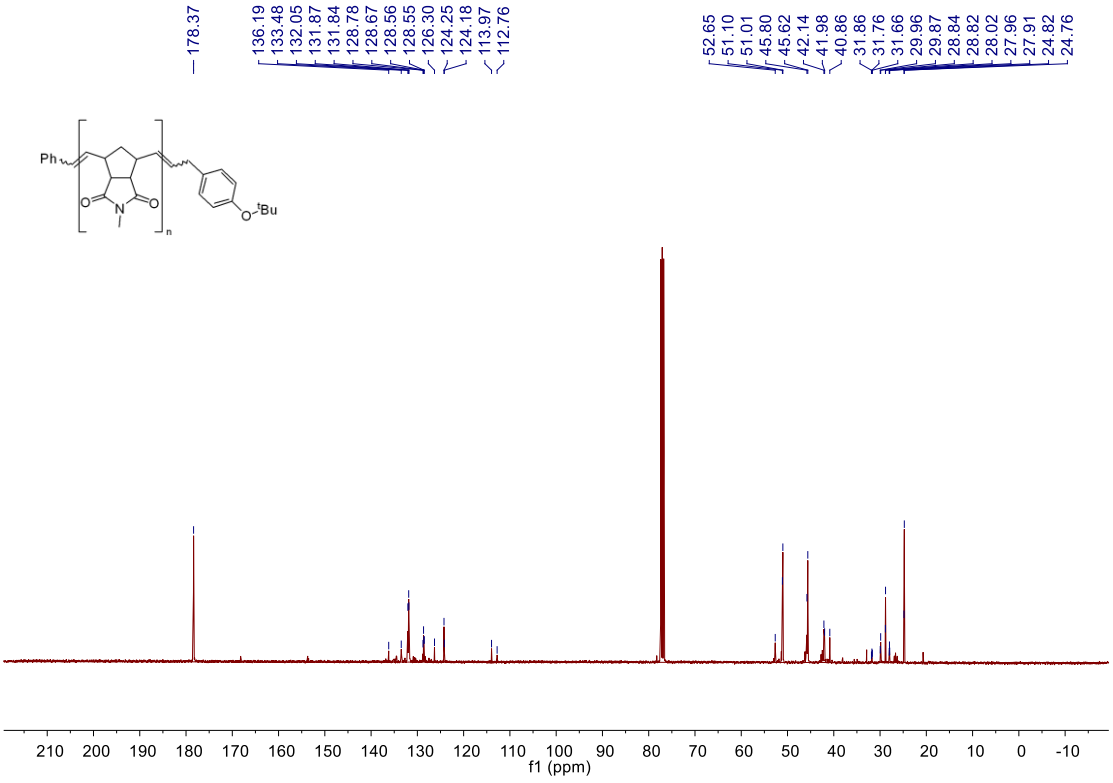

Figure S25 ^{13}C-NMR spectrum(101 MHz, $CDCl_3$) of **Polymer 6**

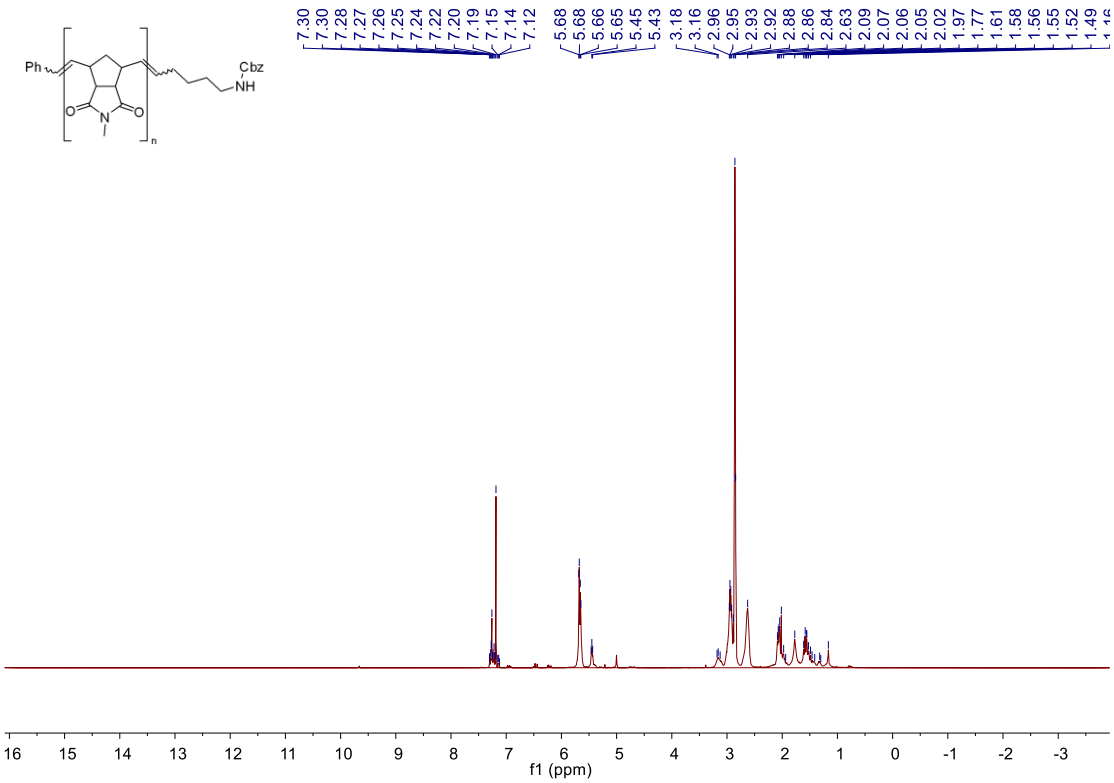

Figure S26 ^{1}H-NMR spectrum(400 MHz, $CDCl_3$) of **Polymer 7**

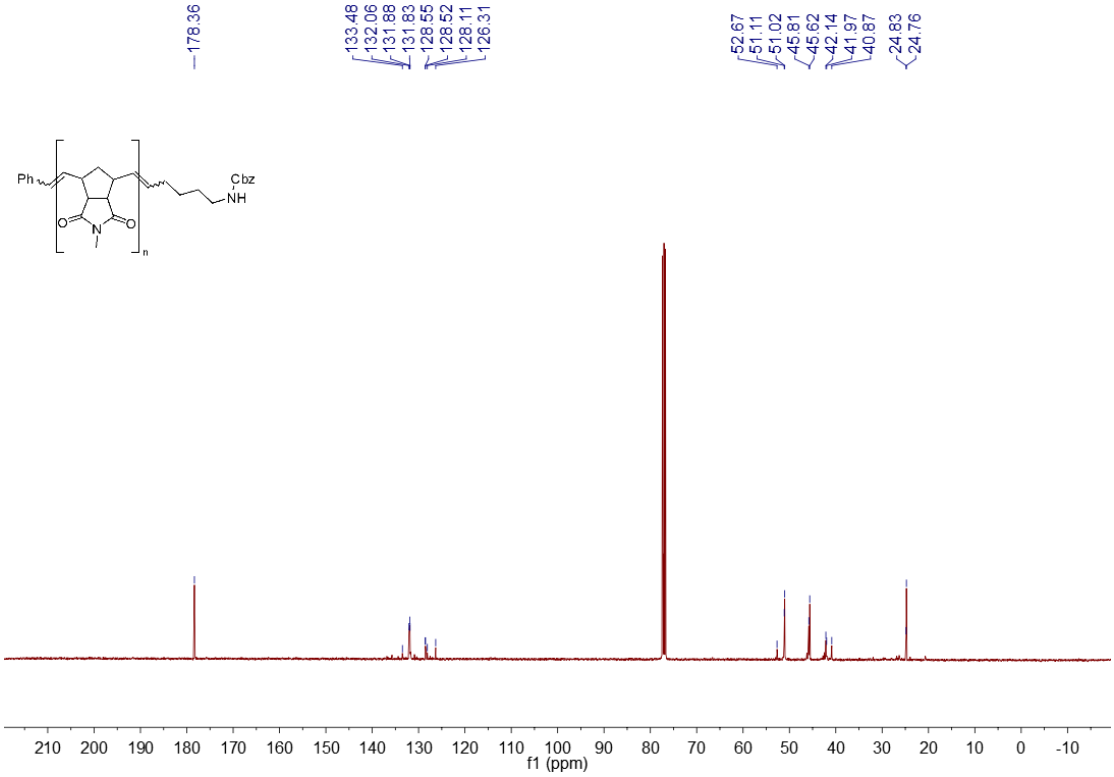

Figure S27 ^{13}C-NMR spectrum(101 MHz, $CDCl_3$) of **Polymer 7**

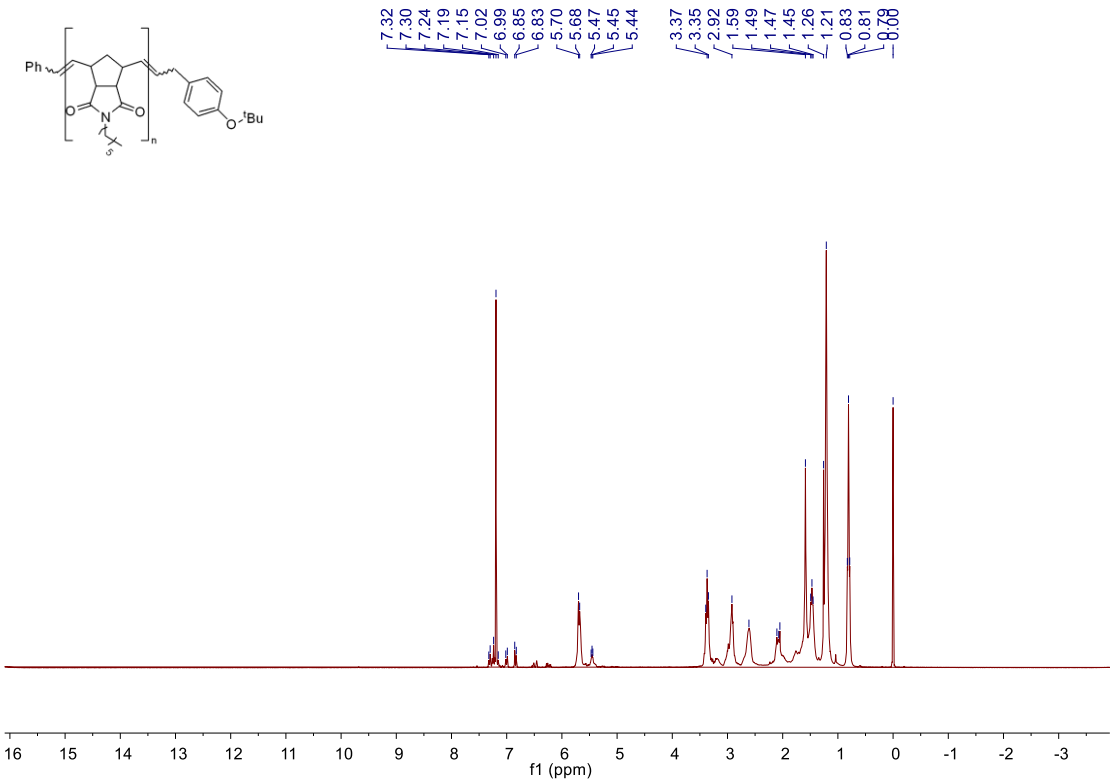

Figure S28 ^{1}H-NMR spectrum(400 MHz, $CDCl_3$) of **Polymer 8**

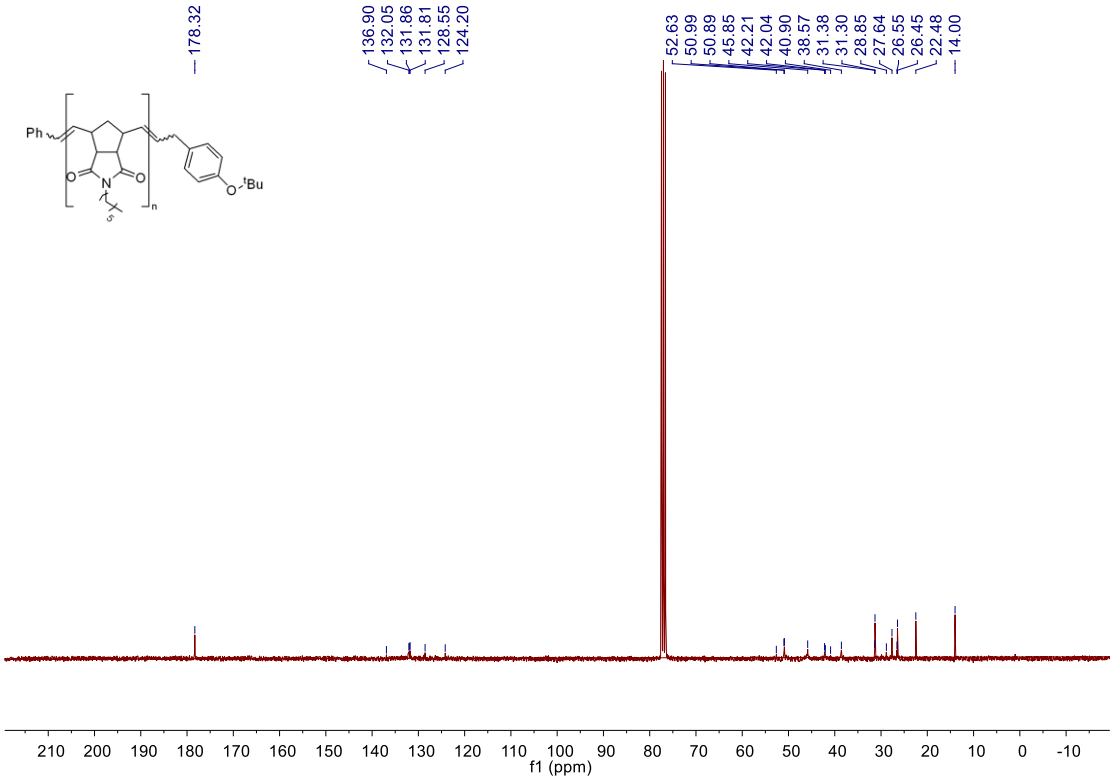

Figure S29 ^{13}C-NMR spectrum(101 MHz, $CDCl_3$) of **Polymer 8**

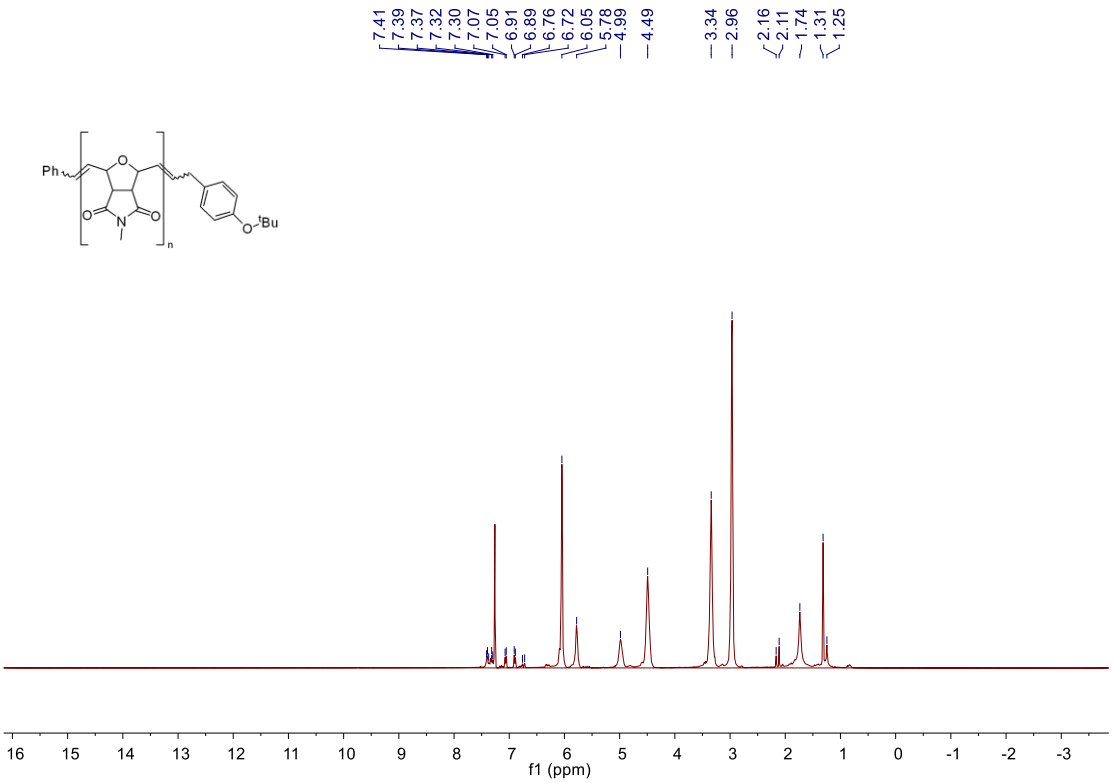

Figure S30 ^{1}H-NMR spectrum(400 MHz, $CDCl_3$) of **Polymer 9**

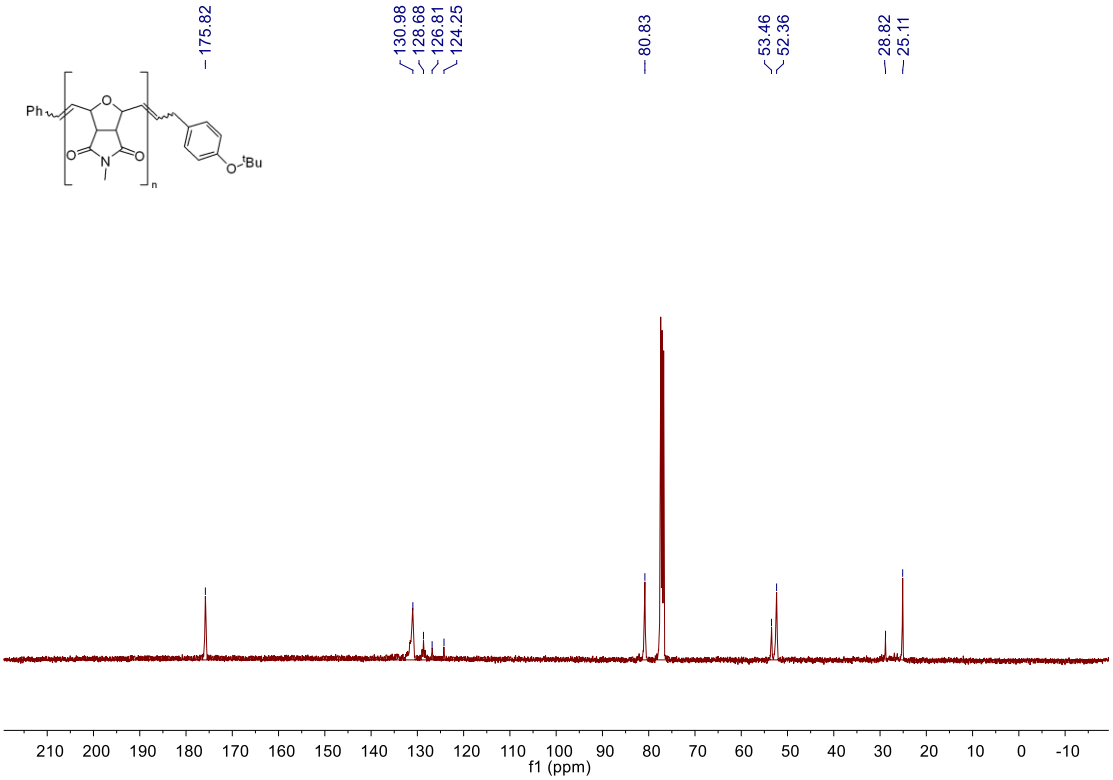

Figure S31 ^{13}C-NMR spectrum(101 MHz, $CDCl_3$) of **Polymer 9**

MALDI-ToF spectrometric data of Polymers

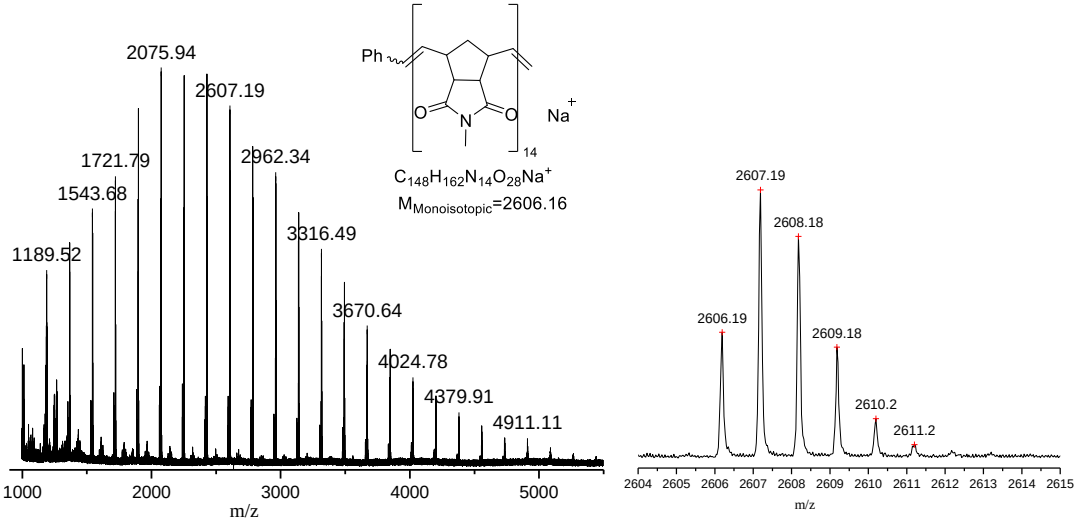

Figure S32 MALDI-ToF mass spectrum (DCTB, NaTFA) of **Polymer 1**

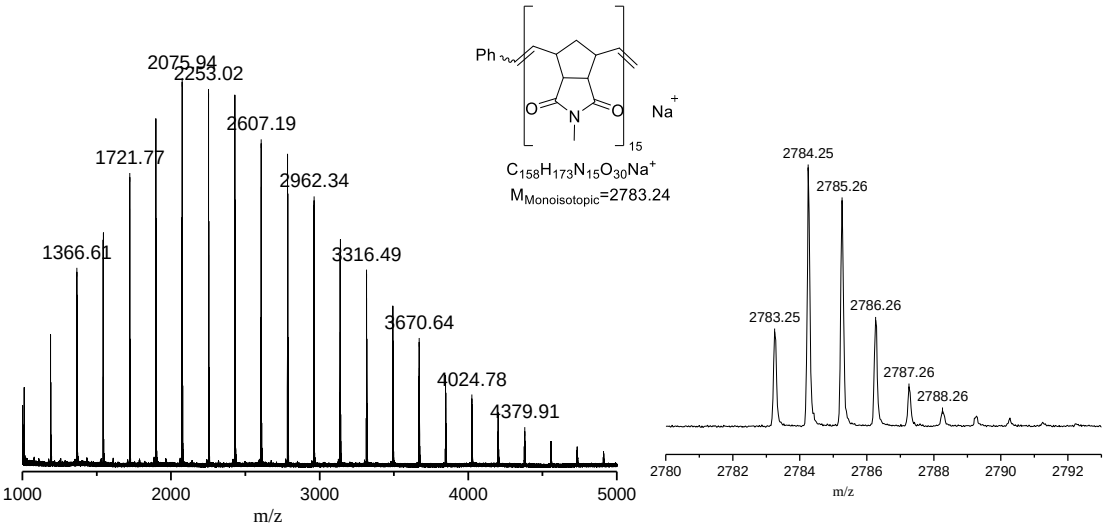

Figure S33 MALDI-ToF mass spectrum(DCTB, NaTFA) of **Polymer 2**

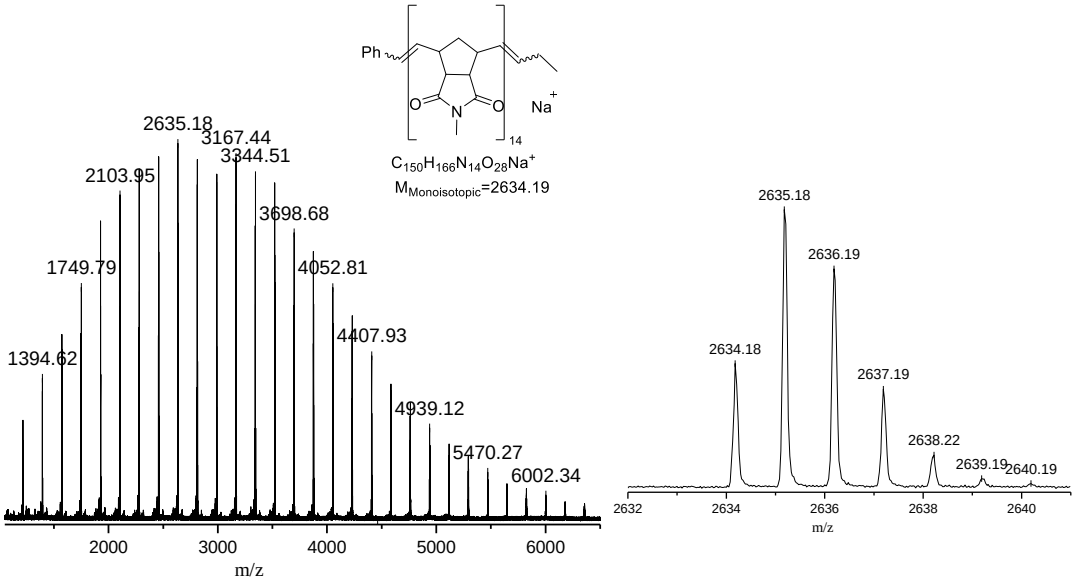

Figure S34 MALDI-ToF mass spectrum(DCTB, NaTFA) of **Polymer 3**

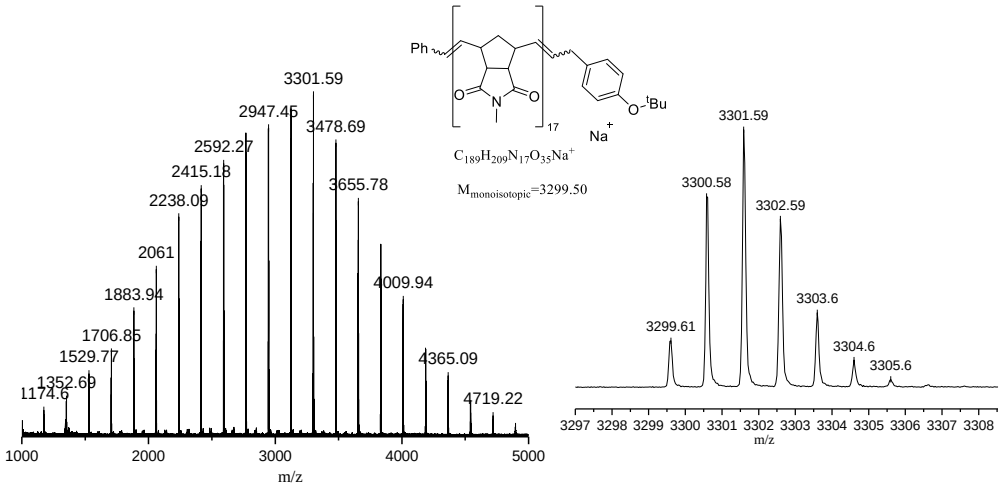

Figure S35 MALDI-ToF mass spectrum(DCTB, NaTFA) of **Polymer 4**

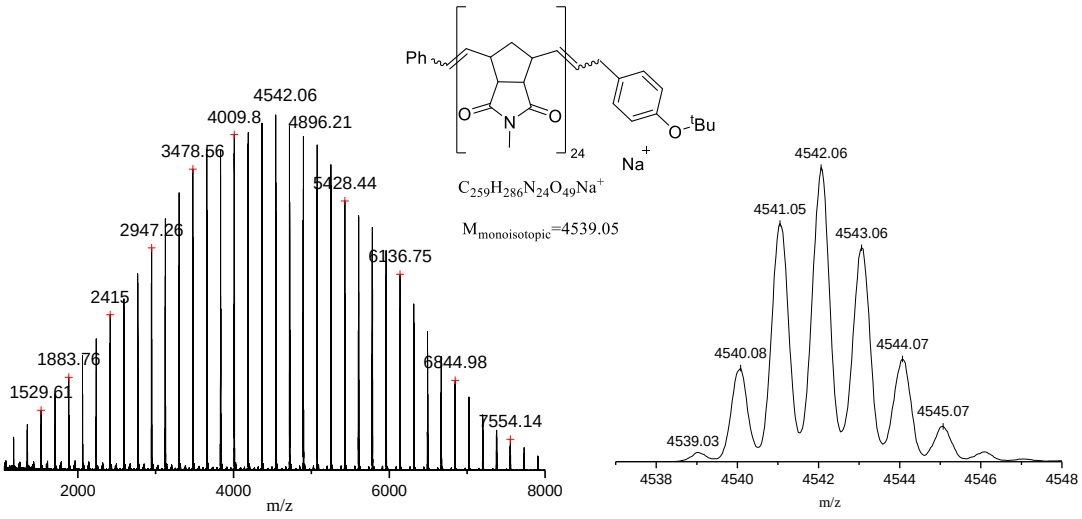

Figure S36 MALDI-ToF mass spectrum(DCTB, NaTFA) of **Polymer 5**

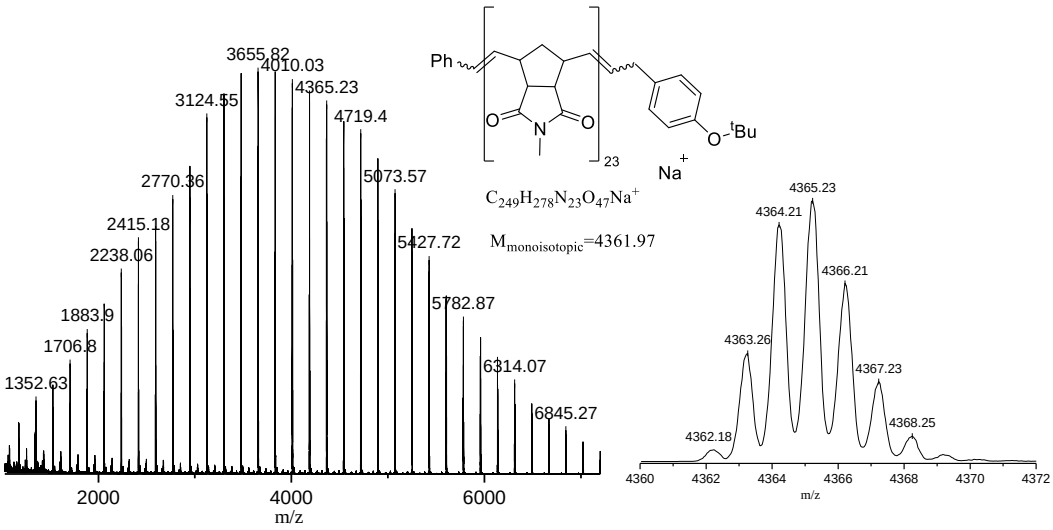

Figure S37 MALDI-ToF mass spectrum(DCTB, NaTFA) of **Polymer 6**

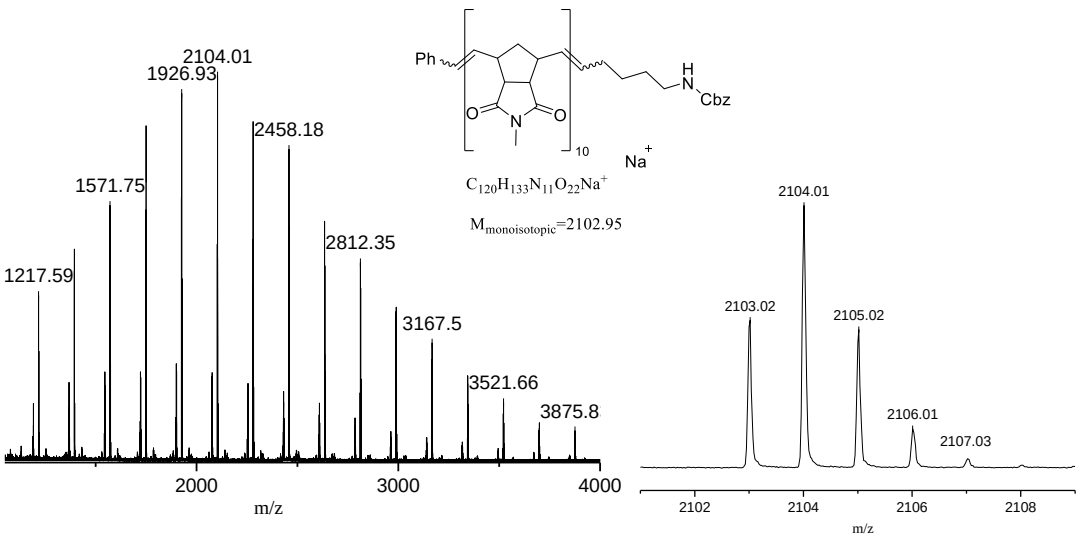

Figure S38 MALDI-ToF mass spectrum(DCTB, NaTFA) of **Polymer 7**

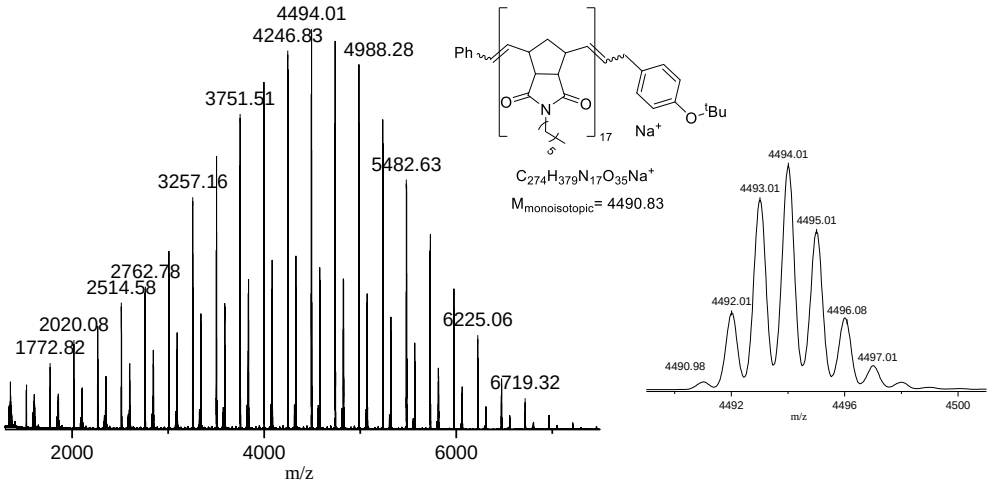

Figure S39 MALDI-ToF mass spectrum(DCTB, NaTFA) of **Polymer 8**

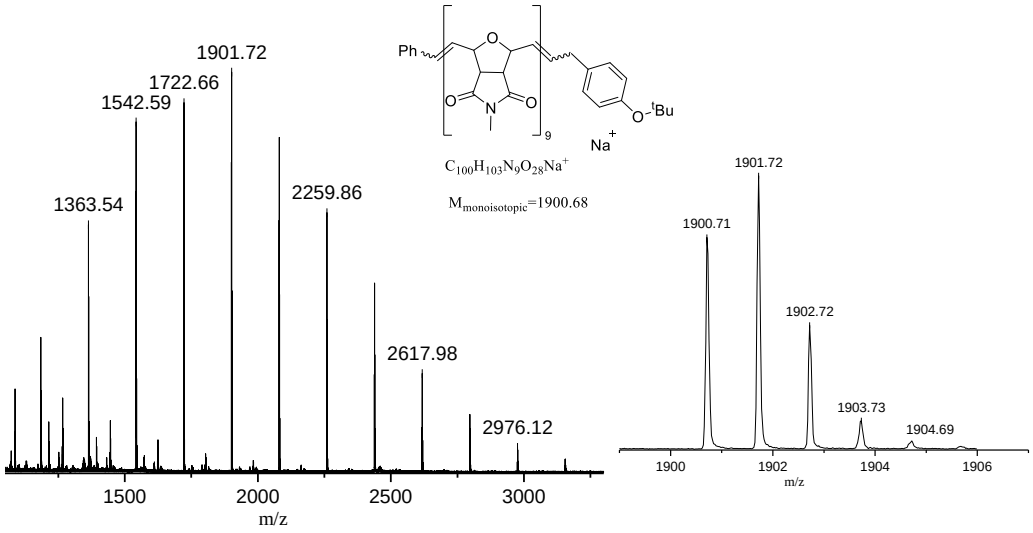

Figure S40 MALDI-ToF mass spectrum(DCTB, NaTFA) of **Polymer 9**

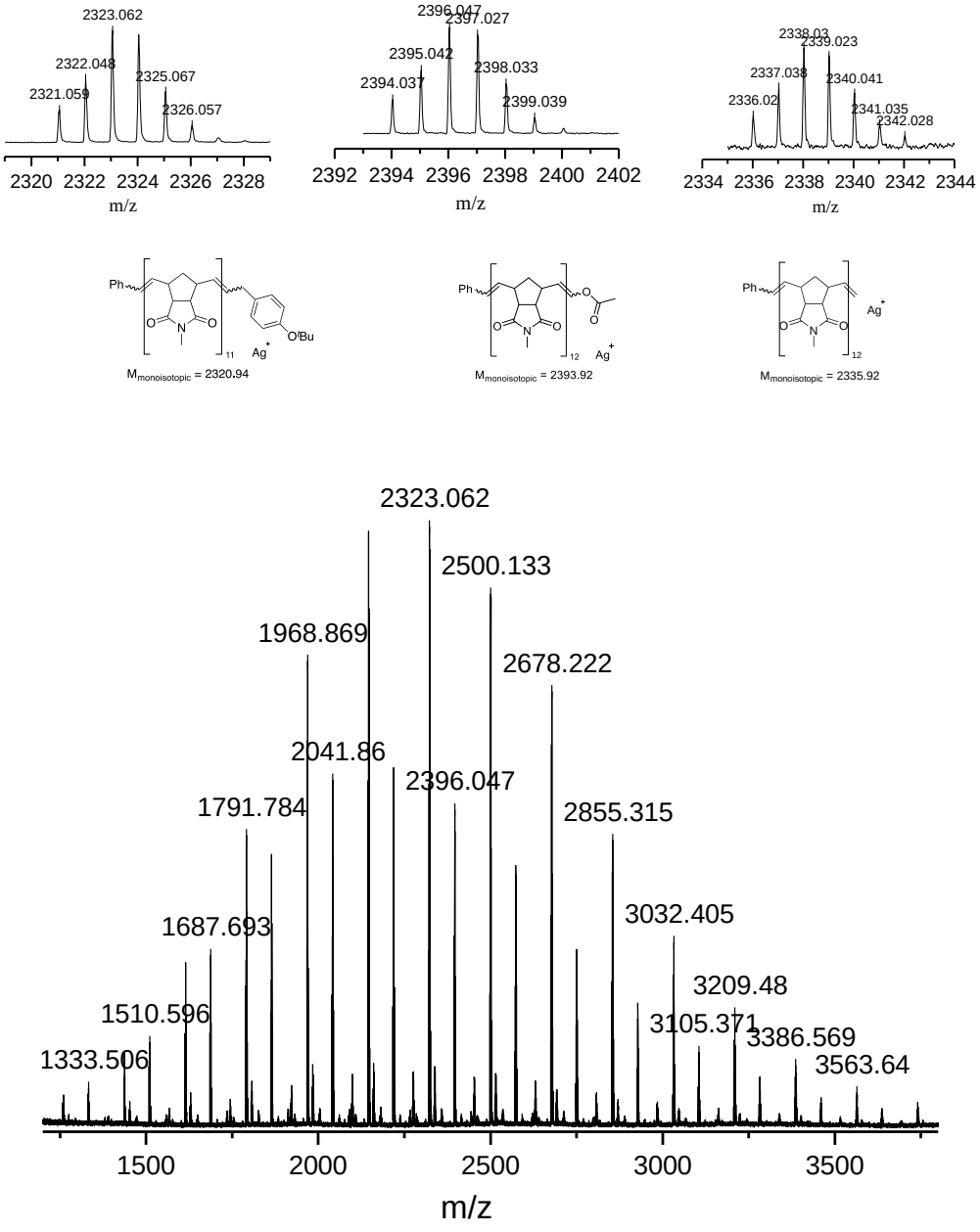

Figure S41 MALDI-ToF mass spectrum(DCTB, AgTFA) of **Polymer 10**

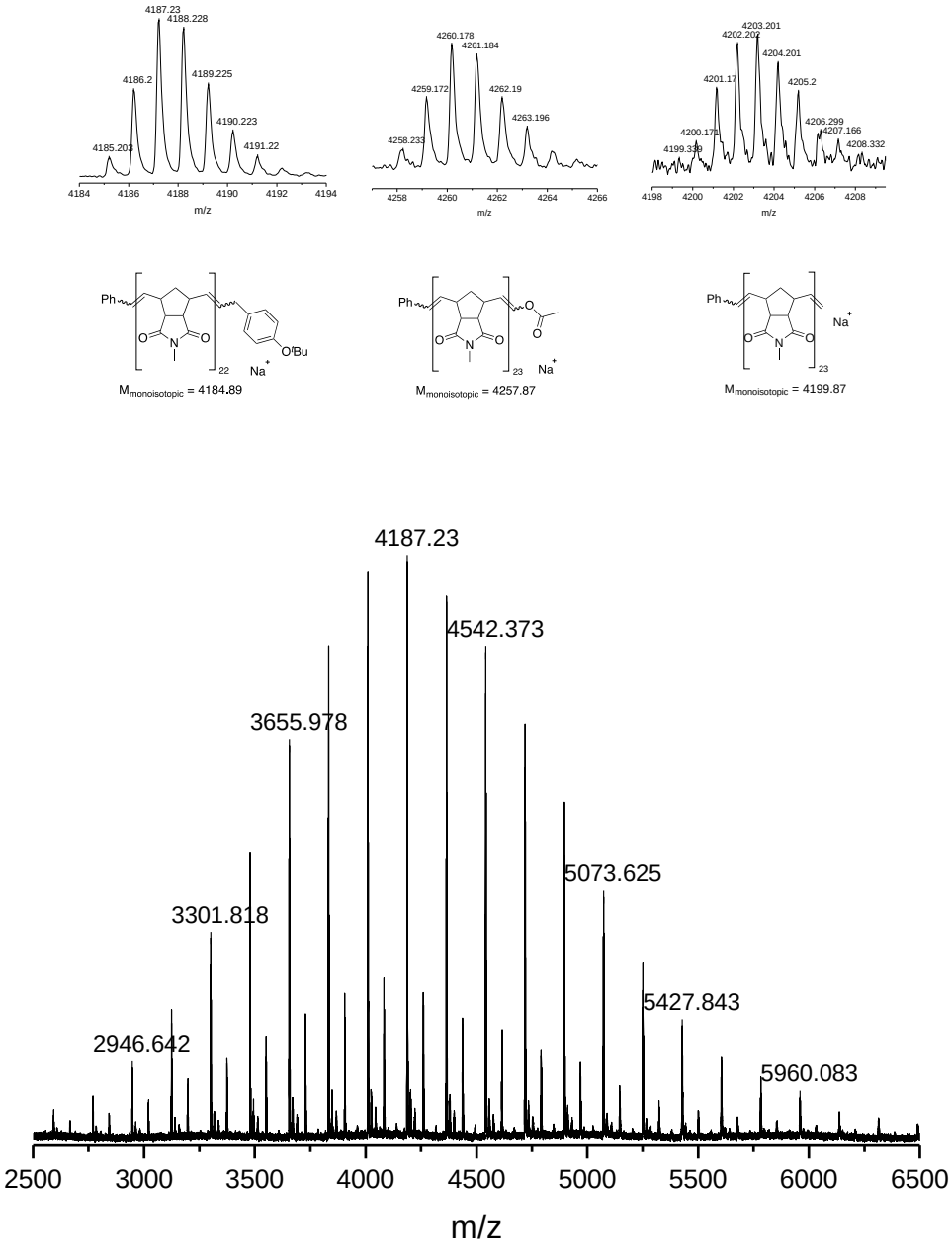

Figure S42 MALDI-ToF mass spectrum(DCTB) of **Polymer 11**

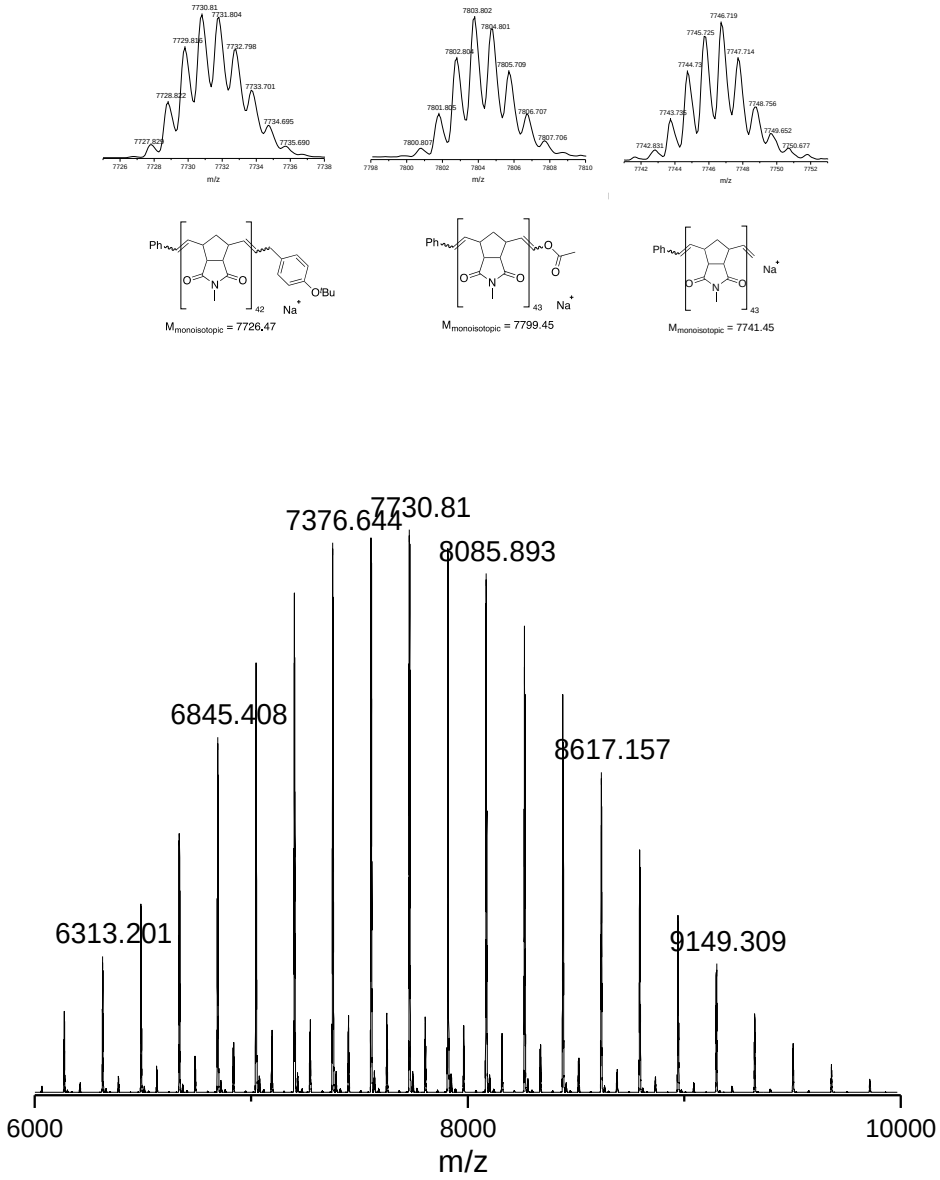

Figure S43 MALDI-ToF mass spectrum(DCTB) of **Polymer 12**

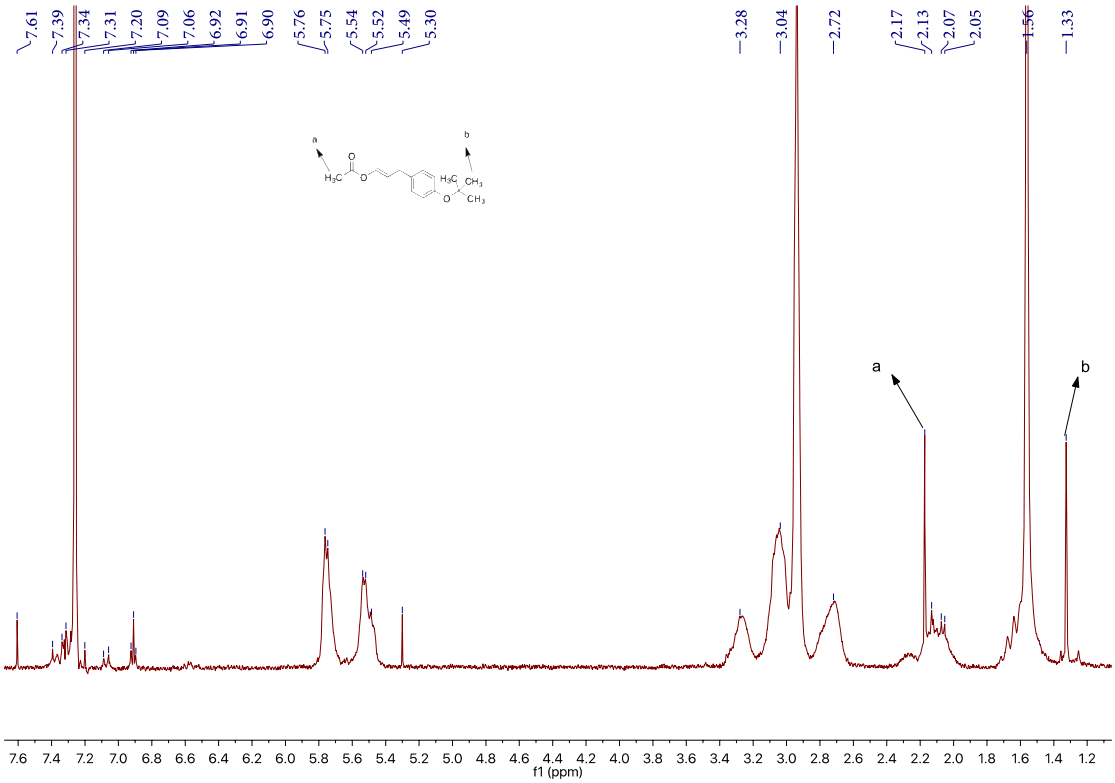

Figure S44 ^{1}H-NMR spectrum(300 MHz, $CDCl_3$) of **Polymer 10**

The polymer end groups corresponding to both, the vinyl acetate (a) as well as the tert.-butyl ether (b) are marked in the spectrum. The inset shows the terminating agent **4**.

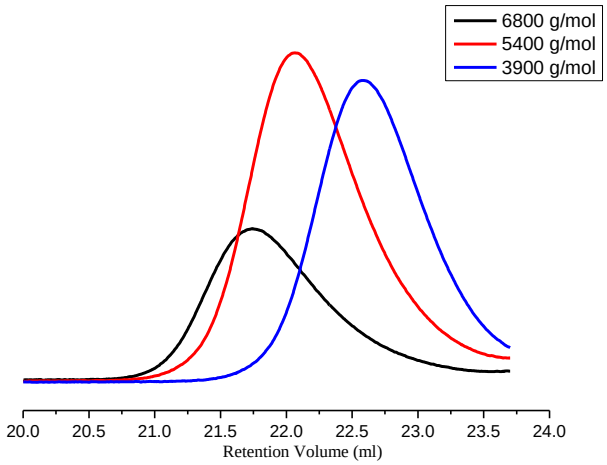

Figure S45 GPC (THF, polystyrene as standards, RI detector) of different molecular weight of **poly(MNI)-Ot-Bu** with **G1**

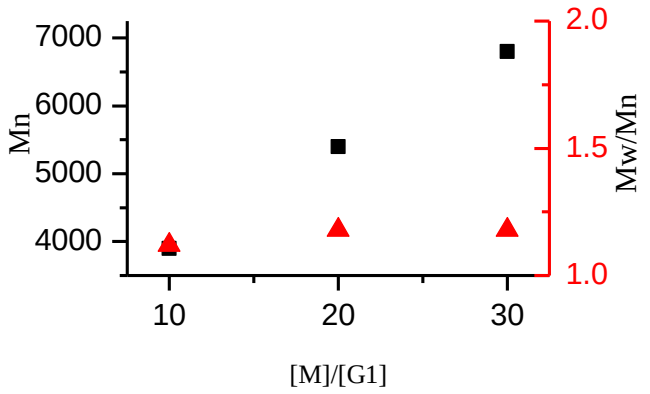

Figure S46 GPC (THF, polystyrene as standards, RI detector) of different molecular weight of **poly(MNI)-Ot-Bu** with G1. "■" = Mn (g/mol) and "▲" = Mw/Mn.

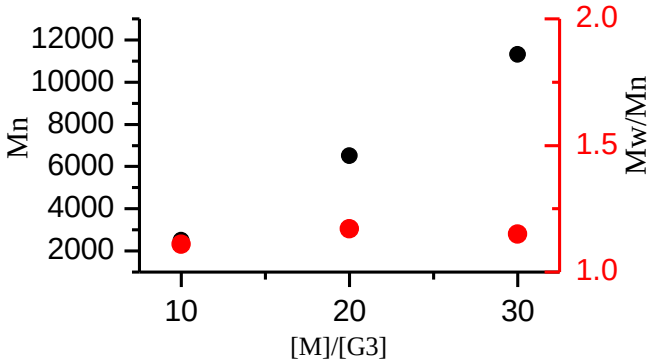

Figure S47 GPC (Chloroform, polystyrene as standard, RI detector) of different molecular weight of **poly(MNI)-Ot-Bu** with G3. "●" = Mn (g/mol) and "●" = Mw/Mn.

References

(1) Bai, Y.; Xing, H.; Lu, Y.; et. al. *ACS Nano* **2015**, *9*, 10227;
(2) Hillmyer, M. A.; Grubbs, R. H.; et. al. *Macromolecules* **1992**, *25*, 3345.